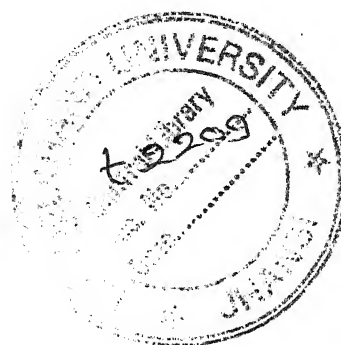


ELECTROCHEMICAL CHARACTERISATION OF THE MEMBRANES



THESIS

Submitted to the

**BUNDELKHAND UNIVERSITY,
JHANSI**

For The Degree Of

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

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CERTIFICATE

This is to certify that the thesis entitled "ELECTROCHEMICAL CHARACTERISATION OF THE MEMBRANES" embodies the original research work of Miss. BHAVANJALI SINGH who has worked under the able guidance and supervision of the undersigned in the post graduate department of Chemistry Bipin Bihari (P.G.) College, Jhansi. The candidate has put more than 200 days in the department as required by the university ordinance. The thesis is suitable for the submission to award the degree of "DOCTOR OF PHILOSOPHY" in chemistry from the Bundelkhand University, Jhansi. Such work has not been submitted to any other university.

Place : Jhansi


(Dr. R.S. Kushwaha)

Date : _____

DECLARATION

I hereby declare that the thesis entitled " ELECTROCHEMICAL CHARACTERISATION OF THE MEMBRANES " being submitted for the degree of "DOCTOR OF PHILOSOPHY" to the Bundelkhand University, Jhansi (U.P.), is an innovative piece of work carried out with utmost dedication by me and to the best of my knowledge and belief that it has not been submitted elsewhere.

Place : Jhansi

Date : _____

Bhavanjali Singh
(Bhavanjali Singh)

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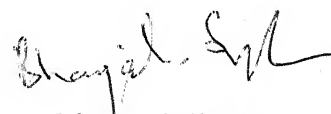
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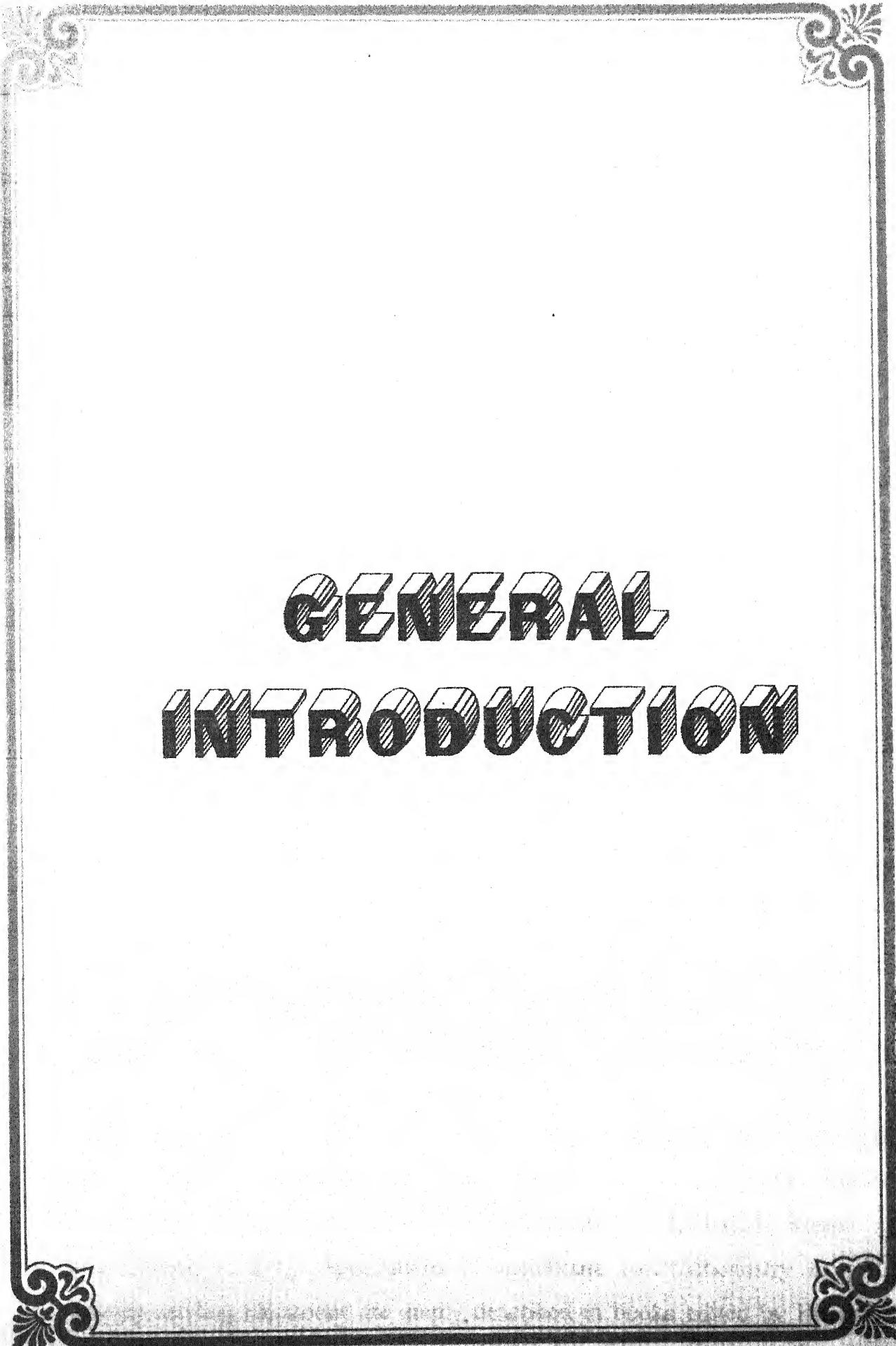
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GENERAL INTRODUCTION

GENERAL INTRODUCTION

Transport processes occurring across artificial membrane separating different solutions have attracted the attention of chemists, chemical engineers and biologists etc. Chemists and chemical engineers would like to understand the mechanisms of transport so that with the knowledge so gained they would be able to fabricate membranes of any desired property or properties. Biologists however, would like to use them as simple models for the physiological membranes in order to understand the behavior of complex cell membranes in terms of established physiochemical principles. The recent progress retaining to membrane diffusion and transport problems have been achieved in varying fields like Chemistry, Biochemistry, Physiology, Pharmacology, Biophysics, and Industrial chemistry etc. in which the starting points and aims have been different. Surface chemistry, Solution theory, Colloid chemistry, Electrochemistry and Thermodynamics etc. have been employed to understand the mechanism of transport in living cells, Desalination and Electronics. There are several areas of membrane research, which has potentially far reaching consequences to medicine and chemical industry. Work in this field is contributing significantly to the economic prosperity and physical well being of all mankind.

The literature in book form describing membrane technology and applications is far too extensive to mention. The principal volume containing significant sections on, or totally devoted to membrane electrochemistry are by Clark and Nachmansohn [1], Helfferich [2], Spiegler [3,4] Merten [5], Marinsky [6], Stein [7], Cole [8], Lakshminarayanaiah [9-11], Hope [12], Arndt and Ropper [13], Plonsey [14], Kotyle and Janacek [15], and others. Continuing series are edited by Bittar [16], Eisenman [17], Darieili, Rosenberg and Cadenhead [18], Applications of membrane electrochemistry to yield activity sensing electrodes are amply described in books edited by Eisenman

[19] and Durst [20] However, this field has produced such a variety of new measuring devices and has opened so many analytical possibilities in terms of new analyses and new detection systems that it is very likely that additional volumes will soon appear. Numerous recent volumes are concerned in part with membrane electrochemistry [21-29].

A precise and complete definition of the word "membrane" is difficult to make [30], and any complete definition given to cover all the facets of membrane behavior will be incomplete. According to Sollner and noble [30-31] "A membrane is a phase or structure interposed between two phases or compartments which obstructs or completely prevents gross mass movement between the latter, but permits passage, with various degrees of restriction, of one or several species or particles from the one to the other or between the two adjacent phases or compartments, and which there by acting as a physicochemical machine transform with various degrees of efficiency according to its nature and composition of the two adjacent phases or compartments. In simple terms it is described as a phase, usually heterogeneous acting as a barrier to the flow of molecular and ionic species present in the liquids and/or vapors contacting the two surfaces [9]. The term heterogeneous has been used to indicate the internal physical structure and external physicochemical performance [30,32-34] From this point of view, most of the membranes in general are to be considered heterogeneous, despite of the fact that, conventionally, membranes prepared from coherent gels have been called homogeneous [35].

The notion of homogeneous vs. heterogeneous membranes proves to be an important distinction from the point of view of mass transport. In the dilute solution limit, the friction coefficients for mass transport by diffusion or migration are inter convertible by Onsager reciprocal relations, and both can be related to jump distances and frequencies according to random walk models. As long as there are no proffered regions of low friction on the membrane, it is

isotropic on a molecular level and is considered to be homogeneous. Uniformity of mesh on a molecular scale is another view of homogeneity. Channel free solid and liquid membranes are usually homogeneous and two phase membrane such as solid crystallites imbedded in a nonionic resin are clearly heterogeneous. The distinction however is not always essential [35].

H.K. Lonsdale, in the editorial [36] reported the wide explanation in order to define the membrane on the behalf of a number of scientists who are engaged in the field of membrane science. According to Webster's New Colligative Dictionary "Membrane", 1. A thin soft pliable sheet is layer of animal or plant origin. 2. A piece of parchment forming part of a roll". Now that is clearly an old and simplistic definition, therefore, in other more sophisticated dictionary, The Mc-Graw Hill dictionary [2nd ed], "The membrane [i] the medium through which the fluid stream is passed for purpose of filtration, [ii] the ion exchange medium used in dialysis, diffusion, osmosis and reserve osmosis and electro dialysis" On the other hand, "a membrane is a thin, usually polymeric film that exhibits perm selectivity". The definition of perm selectivity might be defined as the property of a membrane characterized by exhibiting a much higher permeability to one species. Patrick Mears, of the department of chemical engineering, university of Exeter, Exeter England who has spent most of his distinguished carrier in the membrane field and who also served on Editorial board of Journal of Membrane Science for more than a decade offers this definition "a membrane can be regarded as phase or group of phases that controls the transport of matter and energy between two essentially uniform phases which it separates. Although one usually thinks of a membrane as thin relative to its other dimension, this is not always so, for example, in the case of hollow fine fibers. A simple formulation of fluxes and forces requires only that end or edge effects and the divergence of flows may be neglected.

During the last few years several reviews [37-39] on the development of membranes and their various separation applications, a comprehensive account

of the state-of-the-art of Reverse Osmosis [RO] membrane has been reported by Channabassappa [38]. Recently, Strathmann [39] has extensively reviewed the latest development of work pertaining to polymeric membranes. Sourirajan [40] has given an exhaustive account of the technological and engineering aspects of the reverse osmosis process. Pusch [41] has reviewed the synthesis of a number of membranes together with their structure and their wide applications.

In actual sense membranes may be solid liquid or gas [42] and the outer phases are usually liquid or solid. Membranes are usually thin in one dimension relative to the other two dimensions. This property is only functional or operational. In order to achieve a measurable chemical change or electrochemical effect and to make chemical or electrochemical measurement on a membrane system in a reasonable time, some transport related property must be susceptible to temporal change. Thus a change in potential flux or concentration [among many varying and measurable quantities] requires membrane thickness d such that $d^2/2D$ is comparable with the observation time [D is a mean diffusion coefficient]. Although irregularly shaped membrane are conceivable, most theories and experiments are restricted to systems with one dimensional or spherical symmetry such that transport occurs in one dimension, the x direction in parallel-face, planar membrane or along a radius in membranes with spherical shape.

Membranes are considered to be porous or nonporous depending upon the extent of solvent penetration [43]. At the nonporous extreme are membranes, which are nonionic and contain negligible transportable species at equilibrium. Ceramics, quartz, anthracene crystals, and Teflon films between metal electrodes or electrolyte bathing solutions are solid membrane examples. Organic liquid films such as hydrocarbons and fluorocarbons in contact with aqueous electrolytes are liquid membrane examples. At the other extreme are porous membranes, which can be solvated and will contain components from

the outer phases. Among these are nonionic films such as cellophane, inorganic gels, and loosely compressed powders in contact with aqueous solutions. These materials absorb solvent from the surrounding media and may also extract other neutral molecules and ionic salts. More widely studied are the membranes of polyelectrolytes, aqueous immiscible organic liquid electrolytes [2,9,11,44], various parchment supported inorganic precipitates [45-56], solid ion conducting electrolytes including silver halides, rare earth fluorides, and alkali silicate and alumino-silicate glasses [19,20,57,58]. All these materials contain ionic or ionizable groups within the membrane, which are capable of transport under diffusion or electric field forces. In addition, these materials possess the property of porosity. Polyelectrolytes tend to swell rapidly by osmotic pressure driven uptake of solvent. Liquid ion exchanges are surprisingly slow to take up water, while the inorganic salts have no tendency to hydrate glass membranes are complicated by simultaneous hydrolysis of the polyelectrolyte during uptake of water [59-61].

Depending on the dielectric constant and solvent penetration, sites are potentially, partially or even completely ionized. A characteristic of electrolyte membrane is the presence of charged sites [2,62-64]. If ionic groups are fixed in a membrane as SO_3^- and COO^- attached to cation exchange resins, the membrane is considered to possess fixed sites, even if protons or metal ions are covalently bonded to the sites. In glasses, the fixed sites are SiO^- and AlO^- groups, while in anion exchange resin membrane these are N^+ . On the other hand liquid ion exchangers, which are water immiscible such as diesters of phosphoric acid, can be viewed as mobile site membrane. The acid is trapped in the organic phase, while the protons and / or other cations can move in and out of the membrane, the phosphonate cannot. Membranes without ionizable groups contain no charge sites. It is important to know that cellulose triacetate which is initially site free, soon develops negative sites by hydrolysis and oxidation on exposure to aqueous solutions.

The frequent use of "charged" and "uncharged" in the membrane literature is usually unsound electro statically, but does provide an intuitive chemical description. For example, "charged" membranes usually refer to electrolyte membrane such as solid and liquid ion exchangers where the fixed and mobile sites are the "charges". Actually these membranes are quasi-electro- neutral in their bulk when the thickness is large compared with the Debye thickness at each interface. Quasi-electro neutrality means that in any volume element charge compared with the distance between ions; the sum of the ionic charges $\sum_i Z_i C_i = 0$. In the literature, "uncharged" membrane are those, like cellophane, with no fixed charges, This frequently used literature definition provides no place for lipid bilayer membranes which are electro statically neutral only in the absence of charge carriers and in the absence of bathing solutions whose salts possess preferential solubility of anion over cation or vice versa, but are usually electro statically charged by an excess of ions of one sign in normal operation. Thick hydrocarbon membrane and membrane of diphenyl ether [or derivatives] phthalate, and sebacate esters are generally neutral in the presence of neutral carrier species which preferentially solubilize ions of one sign. The use of "charged" and 'uncharged' to describe electrolyte or non-electrolyte membrane has been discouraged unless the precise electrostatic connotation is involved [35].

Membranes may broadly be classified into natural and artificial. Natural membranes are classified to possess of fundamental unit membrane structure which is a bimolecular leaflet of lipid with their polar groups oriented towards the two aqueous phases of the cell, and protein is supposed to exist close to the polar heads of the leaflet. This type of the universal

structure is absent in artificial membranes. Eisenmann et al. [65] have given a classification of these membranes based on their structures. However, many of the processes occurring in nature involve membrane transport. Some of the functions performed by such membranes appear to be unique as well as efficient and it would be possible to make synthetic membrane having similar properties. On the other hand when developing a synthetic membrane to perform a certain function one should first attempt to discover if such a process also occur in the nature. If it does, then an advantage can be gained by attempting to mimic the natural membranes. Thus by understanding the natural membrane, one may be able to produce a much more efficient synthetic ones. This use of biological ideas for the development of synthetic membranes has been discussed [66].

Unlike the classification based on membrane structure, membranes are usually classified either on the basis of their nature i.e. coherent gel or otherwise or on the nature of the chemical reaction involved in their formation i.e. addition or condensation reaction. The efforts of various workers have been directed towards: [a] Preparing membranes with good chemical and mechanical stability for fundamental transport studies and for applications in some industrial operation such as the treatment of the brackish water, saline water conversion etc., [b] Building suitable models to mimic the properties of natural membranes, and [c] Preparing composite membranes containing cationic and anionic groups in suitable arrangement to demonstrate and to study the physicochemical phenomena associated with the rectification of alternating current and other special membranes for specific purposes. It is worth while to mention that most of the work

concerning category [A] seems to be directed towards finding suitable membrane material for fabricating a structure for effective desalting sea water by application of pressure. The most commonly used material for casting a membrane for desalination is cellulose acetate although, polymethacrylic acid [PMA] phenolsulphonic acid [PSA], polystyrene sulphonic acid [PSSA] and cellulose esters have proved very useful [67]. A number of investigators in recent years have prepared membrane from cellulose acetate under varying conditions and used them to understand the mechanism of water flow [3,4,5,68-82]. In category [B] bilayer membranes, first generated by Mueller [83], have most widely been used as model for living cells and the studies have given somewhat a better understanding of the structure and function of the natural membranes. The membranes of category [C] are quite numerous [10,35,84-86].

Theories on the transport of charged or uncharged particles across membranes can be roughly divided according to Schlögl [88] into the following groups.

Group one considers the membrane as a surface of discontinuity setting up different resistances to the passages of the various molecular or ionic species [89,90]. The driving forces are the differences of the general chemical potential between the two outer media [differences of pressure or electrical chemical potential are included in the general chemical potential].

Group two considers the membrane as a quasi-homogeneous intermediate phase of finite thickness in which the local gradients of the general chemical potential act as driving forces [62,63,90-96]. Convection may also contribute to particle transport within the membrane.

Group three considers the membrane as a series of potential energy barriers lying one behind the other thus forming, in contrast to group two an inhomogeneous intermediate phase [97-99]. An irregular spatial lattice is formed due to the higher probability of finding a particle in the positions between the activation thresholds. The driving forces arise from the differences between the transition probabilities in opposite directions perpendicular to the membrane.

This grouping attempts to classify the various mathematical approaches, according to the ideal models on which they are based. It is in fact too schematic, as many theories occupy intermediate positions. No author is likely to take the view that one of these treatments is right and the others wrong. The various descriptions supplement each other, and depending on the system under consideration, one of the three will prove the most suitable. It may be shown, for example, that when the number of activation thresholds becomes very large, and the distance between the lattice points sufficiently small, then groups 3 and 2 merge into each other. A transition is also found between groups 1 and 2 [87].

Unlike group 3, groups 1 and 2 can be classified in the general scheme of irreversible thermodynamics. In-group 1 as well as in group 2, linear relationships are assumed between the particle fluxes and the driving forces. Owing to the differing characters of the driving forces, group 1 is treated according to the method of "discontinuous system", and group 2 according to that of "continuous system". Integration in-group 2 across the membrane does not as a rule yield a linear relationship between the flux and the general chemical potential differences. Only for sufficiently small differences does

group 2 merge into group 1 after integration. In this sense group 2 is more general than group 1. Group 2 is, however, inferior to group 1 in that a number of idealizations must be assumed before an explicit integration can be affected. Kirwood [100] finds a correction between group 1 and 2. His initial flux equation differs from that normally used in the treatment of "continuous system " in irreversible thermodynamics. This treatment of Kirwood has been developed and modified by Schlögl [87]. On a broad basis, it may be said that the theories of group 1 are based on the ideas of classical thermodynamics or quasi-thermodynamics, which is restricted to the isothermal systems. The theories of group 2, apart from being more rigorous and realistic allow a better description and understanding of transport phenomena in membranes and are useful in dealing with non-isothermal system. The theories of group 3 provide a general and unified view applicable to systems of differing degrees of complexity. Many of the theories based on the Nernst-Planck flux equation are placed in the first group where as those dealing with the principles of irreversible thermodynamics and the theories of absolute reaction rates are placed in the 2nd and 3rd groups respectively.

The theories of the first group have the advantage of being relatively simple. For ion-exchange membranes, however, they are often inadequate. These theories deal chiefly with processes occurring within the membrane. For such a purpose the theories of the second group are proper choice.

The most important theories of the second group are based either on quasi-thermodynamics or on thermodynamics of irreversible processes. The

fundamental differences between these two approachment are summarized below.

Quasi-thermodynamics is not interested in particle fluxes. One might say that the quasi-thermodynamics approach consists in taking a snapshot of the system and calculating the e.m.f. from the charge which a reversible electric current would produce in the system if it were "frozen" in the state in which the photographic picture was taken. This procedure gives directly the e.m.f. of the cell. No model is needed. Taking the snapshot, however, is often not as simple as it may seem. A rigorous treatment would require the knowledge of the composition of every differential layer of the diffusion zone [i.e., the concentration profiles of all species]. Since obtaining this information experimentally is usually too lengthy task or even quite impossible, the quasi-thermodynamic treatment is forced to make assumption about the condition of the system.

The thermodynamics of irreversible processes [101] in contrast to quasi-thermodynamics does not require prior knowledge of the concentration profiles. The set of equations of thermodynamics of irreversible processes interrelates all occurring "fluxes" [of species electric current, heat etc.] and 'driving forces' [gradients of chemical potential, electric potential, temperature etc.]. From measurements of a sufficient number of "phenomenological coefficients", all fluxes and forces and hence also the e.m.f. can be calculated, without knowledge of the profiles and without using the concept of "reversible energy production " on which quasi-thermodynamics is based. Furthermore, thermodynamics of irreversible processes is applicable also to non-isothermal system and includes coupling

of fluxes, which is not covered by quasi-thermodynamics. It may be mentioned here that the discipline of irreversible thermodynamics provides a precise mathematical description of the processes of transport and diffusion in membrane systems. Its application to membrane processes is a natural development of the basic theory of Onsager [102] and has been developed by Staverman [89], Kedem [103] Katchalsky [101], Caplan [104], Mears [105], Spiegler [3,4] Rastogi [106], and others in an extensive and expanding literature.

The theory of absolute reaction rate has been applied to diffusion process in membrane by several investigators. Zwolinski, Eyring and Reese [99] considered the diffusion process as one of the basic phenomena for sustaining the growth and development of plants and organisms. They presented a detailed kinetic approach to diffusion, which clarifies much-established concepts and provide impetus to a fresh approach to the problem in the field of biological diffusion. The absolute reaction rates theory treatment of diffusion and membrane permeability provides a general unified point of view applicable to systems of varying degrees of complexity. It is equally adoptable to the treatment of the permeability of membranes to electrolytes, to non-electrolytes under the driving forces of a concentration gradient, activity gradient, and external and interval potential gradients. Zwolinski, Eysring and Reese [99] treatise on membrane diffusion is based on the "activated state" or the "transition state" theory.

Laidler and Shuler [98] have also treated the kinetics of membrane transport under steady state conditions. They employed similar principles and expressed the rate constant of the overall process of surface penetration

in terms of a number of specific rate constants. Various special cases are considered and discussed with reference to the experimental data. They developed flux equations for solvent and solute especially as a function of the osmotic and hydrostatic pressure across the membrane. Recently, Tien and Ting [107] have applied the theory of absolute reaction rates to diffusion processes through Bilayer Lipid Membranes [BLM] and have derived various thermodynamic quantities like free energy of activation, enthalpy and entropy of activation etc.

Application of electrochemistry in membrane studies is pertinent at three levels [35]. One is the development of techniques with application to experimental phenomenology including current- voltage-time-concentration behavior. A second is the mathematical modeling implied by experiment and tested against experiment. The third level is experimental verification of models in terms of the molecular processes and properties and includes determination of theoretical parameters by electrical methods and by complementary non-electrochemical methods: Physical, Optical, ESR, NMR, Raman, Fluorescence, T-Jump techniques, etc. From transient and steady state measurement of current or membrane potential as a function of chemical composition, chemical treatment, and temperature, the roles of kinetic and equilibrium parameters can be deduced or inferred. A possible approach to modeling begins with the assumption of the membrane as a linear system to which laws of network theory may be applied. Another begins by the solution of basic electro diffusion laws of transport with equilibrium or Kinetic boundary conditions in order to deduce forms for system functions, which satisfy the data.

The most important contribution of electrochemists to membrane electrochemistry is the transfer of perspective and wisdom to the new area. There are many sine qua nons in electrochemistry, which have occurred through extensive studies of electrolytes and electrolyte/membrane interfaces. Electrochemists have learned to subdivide systems into interfacial and bulk processes and to effects of dielectric constant [couple formation, ion pairing], effects of short range forces [adsorption of charged and uncharged species with possibly, changes in rates of interfacial processes], effects of high fields near surfaces [Wien effects, and dielectric saturation], and the important effect of local potentials on rates of interfacial processes [irreversible charge transfers, psi effects, etc.]. In as much as the presence of the space charge at interfaces is a natural consequence of the continuity of potential from one phase to another, the presence of space charge and space charge mediated effects in membrane systems is anticipated.

The earliest efforts towards developing a membrane model were by Michaelis [108], who considered that the change on the membrane was due to adsorption of one kind of ion. Later Teorell [62] and Meyer and Sievers [63] developed a theory of membranes with charges fixed in the lattice. In the Teorell- Meyer-Sievers [TMS] theory there is an equilibrium process at each solution membrane interface, which has formed analogy with the Donnan equilibrium. In addition there is an internal salt diffusion potential, which was first represented by the Henderson equation and later by the more nearly correct expression Lakshmi narayanaiah and Siddiqi [109]. Further assumptions made are [a] the cation and anion mobility and fixed charge concentration are constant throughout the membrane phase and are

independent of the salt concentration and [b] the transference of water may be neglected. The implications of these assumptions have been discussed by Hills, Jacobs and Lakshminarayanan [110]. Charged membranes [111] are normally of three types; [1] negatively charged membranes, [2] Positively charged membrane and [3] Bipolar [62], membrane.

Teorell-Meyer-Sievers [62,63] obtained a mathematical expression for the E.M.F. across a membrane by integrating the Nernst-Planck equation for the diffusion of ions within a membrane, and subsequently adding two phase-boundary [Donnan] potentials to the intermembrane diffusion potential. In deriving the TMS theory, the following three assumptions were made, [a] all ion species both in membrane phase and in the external solutions behave ideally, [b] the ratio of mobility of positive ions to negative ions is constant throughout the membrane and [c] the effect of mass movement is negligible. Various changes have been proposed to correct this defect [110,111], but no satisfactory theory was proposed until the non-ideality of small ions in the membrane was taken into consideration. Various investigators examined the TMS theory and its various refinements critically, both theoretically and experimentally. It was concluded that neither the TMS theory nor its refinements are capable of explaining experimental results obtained from imperfectly perm selective membrane.

Nagasawa and Kobatake [112-115] approached the problem of membrane potentials from the point of view of the theory of rate processes. They have taken the structure of the membrane into account and by applications of the Poisson-Boltzmann equation have computed ionic concentration in the membrane phase.

Again Kobatake et al. [116-118] gave an equation for the electric potential [membrane potential] which arises between two solutions of a 1:1 electrolyte that are separated by an ionizable membrane. The following assumptions were incorporated in the derivation: [a] the activity coefficients γ_+ and γ_- , for mobile positive and negative ions in the membrane phase are represented when the membrane is ionized negatively, by the equation

$$\gamma_+ = \frac{C}{C + X} \quad \gamma_- = 1$$

Where C is the molal concentration of mobile negative ions, i.e., the coions in the present case, in a volume element of the membrane and X is the thermodynamically effective fixed charge density. The molar mobilities, U_+ and V_- , of mobile positive and negative ions are independent of ion concentration.

Bi-ionic potential

A steady electromotive force of a bi-ionic cell containing two electrolytes $A^+ Y^-$ and $B^+ Y^-$ separated by a membrane is called the bi-ionic potential [BIP]. This potential is a measure for the selectivity of the membrane for the ions of the same sign and has been the subject of many theoretical and experimental studies [119-123]. The mathematically rigorous equations were derived on the basis of the thermodynamics of irreversible

process by Scatchard [98] and Helfferich [123]. In their derivations, however, they considered only a perfectly cation selective membrane separating two mixtures of 1:1 electrolyte with a common anion, i.e., neglected the effect of flow of anion of the BIP. Moreover, these types of treatment did not provide information about the actual mechanism, which produces, observed BIP for the membrane, which arises between solutions of an electrolyte of different concentration separated by a uniform membrane. Teorell-Meyer-Sievers [TMS] [62,63] derived a first theoretical equation based on the fixed charge membrane model. After that Toyoshima [118] also integrated flow equations provided by the thermodynamics of irreversible processes under the appropriate assumptions for the mobilities and activity coefficients of small ions in the membrane phase to derive an equation for the membrane potential and found the derived equation agreed with typical experimental data with porous membranes covering wide ranges of concentrations of external solutions.

Impedance

Numerous investigations [124-129] particularly on living membranes, with alternating currents have shown that they exhibit a composite resistance i.e. impedance, which is different at different frequencies of the current employed. Plain electrolyte solutions, on the other hand, show a frequently independent resistance. The impedance of the membrane has been resolved into a 'resistances' term [of the ohmic type] and a 'reactance', the later being usually regarded as due to a 'capacity'

residing in the membrane structure. Many speculations have been devoted to the significances of these impedance terms. Although it is true that the impedance methods have offered excellent service in permeability research as sensitive indicators that 'something has happened' it is regrettable that no convincing or complete view of its theoretical background has as yet been put forward. A common interpretation has been that the resistance term is connected with the ion permeable parts [lipoid layers etc.] of the membrane of tissues investigated.

The systems under investigation are parchment supported inorganic precipitate membrane of [1] Nickel sulphide and [2] Cobalt sulphide for the studies of their transport properties of metal ions, are reported for the Ph.D. thesis. The membrane electrolyte system has been considered to contain four chemical species, concentration 1, co-ion 2, water 3, and 4th the membrane matrix, which carries fixed inorganic groups and excludes the possibility of chemical reaction within the membrane. The membrane matrix has, therefore, been considered to consist of fixed charge and adjacent polymer segment, which together constitute the repeat unit of the matrix. It is, therefore, possible that Kinetic-coupling interaction of membrane matrix will include not only the contribution of fixed charge, but also specific polymer effects if such exist. This is an important qualification to the description of the four species as simply as ion, although it appears from earlier studies that such effects are small [130-132].

The discussion has mainly been restricted to commenting on only a few points concerning the following ionic processes in the membrane system, "permeability phenomena".

- 1- Ionic transport "flux"
- 2- Membrane potential
- 3- Electrical conductivity
- 4- Ionic distribution equilibria
- 5- Spatial distribution of ions and the potential within the membrane,

The thesis has been presented under the following heads:

1- DISSOLUTION OF ELECTROLYTES:

Under this head the evaluation of diffusion rates of a number of 1:1, 2:1 and 3:1 electrolytes through parchment supported cobalt and nickel sulphide membranes at different concentrations diffusion coefficient and various thermodynamic parameter have been calculated in order to understand the mechanism of ion permeation through the membranes.

2- MEMBRANE CHARGE DENSITY:

This portion deals with the measurements of membrane potential across parchment supported cobalt and Nickel sulphide membranes using separately various 1:1 electrolytes at different concentrations under isothermal condition for the evaluation of thermodynamically effective fixed charge density of the membranes as well as to examine the validity of the recently developed theories for membrane potential including those based on the thermodynamics of irreversible processes.

3- MEMBRANE SELECTIVITY:

This portion deals with the evaluation of membrane selectivity of parchment supported nickel and cobalt sulphide membranes towards the metal ions from bi-ionic and multi-ionic potential measurements for various 1:1 electrolyte systems. The experimentally observed values of membrane conductance for the same electrolyte systems are also actively involved to establish the selectivity order of metal ions in the membrane phase. The values of thermodynamic activation parameters evaluated using absolute reaction rate theories are included in the support of the membrane selectivity order of metal ions.

REFERENCE

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CHAPTER-1

DIFFUSION OF ELECTROLYTES

INTRODUCTION

The transport of chemical species across synthetic and biological membranes is of great interest in many areas, ranging from, for example, separation [1] membrane supported reaction [2] and gas permeation [3] to life science application such as transdermal drug delivery [4]. In many cases transport measurements are averaged over the whole [or a large section of] the membrane. When correlation is made between the rate of transport and the structure of the membrane, the latter is often from *ex Situ* microscopy studies. Further more, the transport process is involve in the membranes as to use then as membrane distillation [M.D.]. In fact it is a membrane process that has long been investigated. In small scale laboratory studies and the potential to become a viable tool for water desalination [5], M.D. is a separation process that combines simultaneous mass and heat transfer through a hydrophobic microporous membrane. The mass transfer in direct contact membrane distillation is three step process involving [i] diffusive transport from the feed stream to the membrane interface [ii] combined diffusive and convective transport of the vapour through the membrane pores, and [iii] condensation of the vapour on the membrane interface on the product side of the membrane

When two electrolyte solutions having different concentrations are separated by a membrane, the mobile species penetrate the membrane and various transport phenomena are induced into the system. The number of forces that may normally operate in the absence of external magnetic and gravitational forces to cause a flow or flux of molecular or ionic species

through it are: [I] difference of chemical potential $\Delta\mu$, [ii] difference of electric potential ΔE , [iii] difference of pressure ΔP , [iv] difference of temperature ΔT . These forces when operate individually or in combination may generate a number of phenomena [6-9]. These are schematically represented in a recent book written by Lakshminarayanaiah [10]. A prerequisite for the success of many operations indicated in the figure is the availability of suitable membrane system. Therefore, considerable attention has been given in recent years to the development of membranes, with particular and predetermined specific properties. A variety of compound and associated processes that have been employed to prepare them and the important literature concerning transport phenomena are described in a number of books [11-15]. A theoretical discussion of many of transport phenomena has been given in a monograph by Schlögl [16] and also appeared in the proceedings published in recent years [17-21].

Transport processes occurring across membranes are of great interest for biologists, who use them as simple models for physiological membranes in order to understand, the behaviour of complex cell membranes in terms of established physicochemical principles. It was demonstrated by Teorcell [22] that the gastric mucosal membrane, in some formal aspects at least behaved exactly like parchment membrane. His further findings that electrolytic transport processes in stomach could be handled by some thing similar to Fick's diffusion law and that Nernst Plank formulae for electrical potential were applicable who encouraged the studies of [a] the assymetric polymeric membranes [23-27] which mimic some of the properties of nerve cells [28,29] as models for biological system and [b] for us to proceed further with

the studies of parchment supported membranes [30-38].

Theories of membrane behaviour, particularly those of complex ions, have been discussed by Kedem and Katchalsky[39] in a series of theoretical papers. The various theories according to Schlögl[40] may be roughly divided into three groups, depending on the nature of the flux equation used in the treatment. Older theories or their modern refinements based on the Nernst-Planck flux equation fall into one group. A second group comprises the theories which use the principle of irreversible thermodynamics. The third group is made up of those theories which utilize the concepts of the theory of rate processes. These have been reviewed in a number of monographs, particularly that of Lakshminarayanaiah [10].

In this chapter, the diffusion rate studies of simple metal ions through parchment supported nickel and cobalt sulphide membranes under isothermal conditions are described. The diffusion rate of the ions have been computed using a simple cell assembly shown in Fig. 1. The advantage of the method is that various membrane parameters namely, membrane resistance R_m , membrane potential E_m and the computed diffusion rate could be known within two three minutes. The method is based on the equation derived by W.W. Kittelberger [48] from the simple laws of electrolysis. The results have been discussed in the light of Eisenman-Sherry model of membrane selectivity [41-43] and the theory of absolute reaction rates [44-46].

EXPERIMENTAL

Parchment supported cobalt and nickel sulphide membranes were prepared by the method of interaction suggested by Kushwaha and co-workers [30,

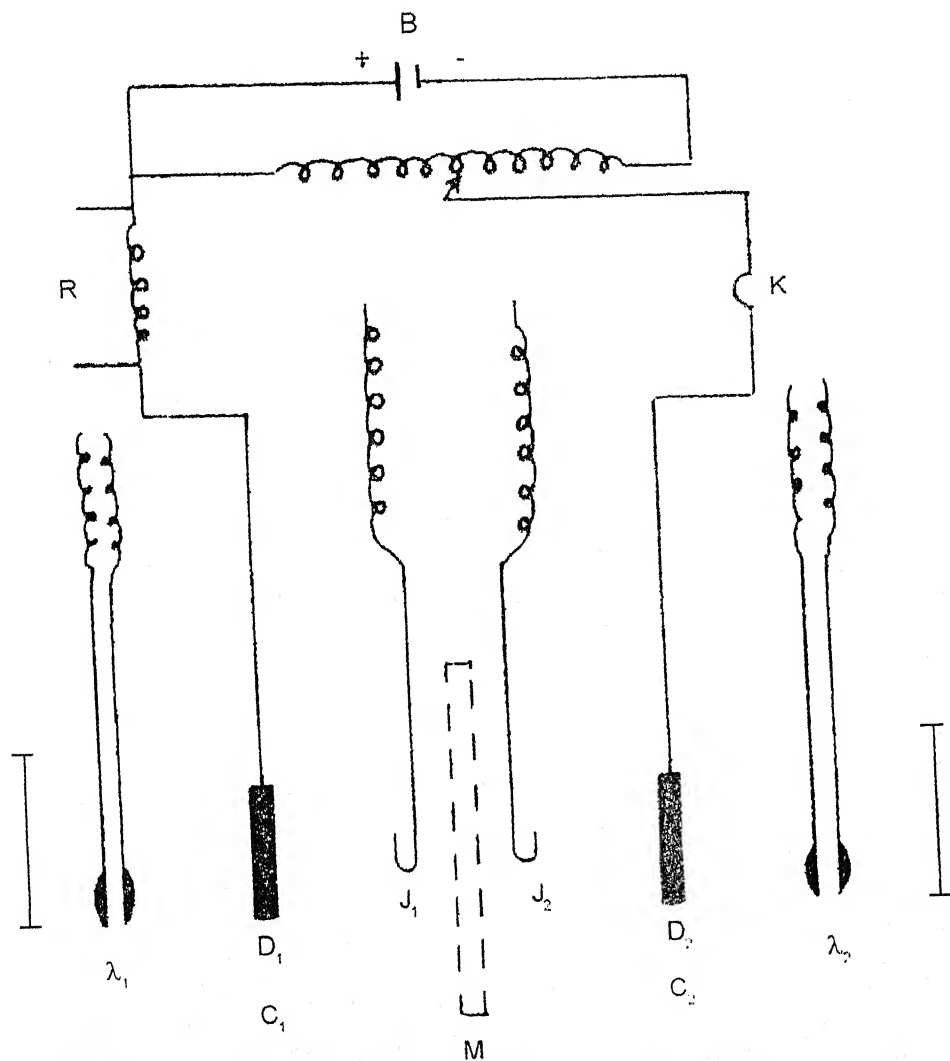


Fig. - 1
ASSEMBLY

31]. To precipitate these substances in the interstices of parchment paper, a 0.2 M solution of sodium sulphide was placed inside a glass tube, to one end of which was tied the parchment paper [supplied by M/s Baired and Tatlock London Ltd.] previously soaked in water. The tube was suspended for 72 hours in a 0.2 M solution of either cobalt [16] or nickel [16] chloride. The two solutions were interchanged later and kept for another 72 hours. The membranes thus prepared were washed with deionized water to remove free electrolytes. It was then clamped between two half cells as shown in Fig. 1. The half cells contained 125 ml of electrolyte solution while the capacity of each of the cell holding the membrane was about 130 ml. Initially these concentrations C_1 and C_2 were 0.001 M and 0.1 M. Each of the half cell was fitted with a conductivity cell [λ_1 and λ_2] firmly fitted to follow concentration changes using conductivity bridge [Cambridge Instrument Co., England.No. 350140] and two anion reversible Ag-AgCl electrodes one a disc type [D_1 , D_2] to pass a small D.C. current and another J-shaped wire electrode [J_1 , J_2] to measure membrane potential following current flow. The solutions in both the half cells were kept well stirred by magnetic stirrers. The whole cell assembly was immersed in a water thermostat maintained at 10°C , 15°C , 20°C and $25^\circ\text{C}[\pm 0.1^\circ\text{C}]$

Exactly known weights or volumes of test solutions were introduced [say at zero time] and the platinized platinum electrodes were connected to the conductivity bridge to follow conductance change with time. No appreciable change in conductance was noted within the 4 hr period on the C_2 side [0.1 M] and so we have assumed this concentration to be practically constant and followed only the conductance change on the C_1 side. The exact

concentration of this solution was determined from a calibration curve where conductance was plotted against concentration.

Another set of calibration curves were also needed to obtain concentration potential E_C + from the plots of e.m.f against $\log f_c$, according to the equation

$$E_{C+} = RT/z_+F \ln f_c \quad [1]$$

using a pair of saturated calomel and Ag-AgCl electrodes in the test solutions on either side of membrane. For all the electrolytes under investigation E_{C+} was taken as the difference between e.m.f. value of the dilute and concentrated solutions.

Membrane resistance was determined by measuring potential across J_1 and J_2 electrodes with and without applying an external e.m.f. to the disc electrodes. The change in potential was taken as E_m . The current I passed through the membrane system was determined by measuring IR drop across a Precision Kilo-ohm resistor. The current was kept very low in order to minimise the ion transfer during the period [2-3 min.] required for each resistance measurements. The direction of current flow was reversed in each successive measurements.

Membrane potentials were evaluated from the electrical potential developed across J_1 and J_2 electrodes when no current was being passed. The total potential E_{obs} developed across J-shaped Ag/AgCl electrodes [J_1 and J_2] is the algebraic sum of electrode potential E_c and membrane potential E_m .

E_C was calculated by the equation

$$E_{\bar{c}} = RT/Z_- F \ln a_2/a_1 \quad [2]$$

and E_m was obtained by subtraction. The thickness of the membranes were as follows:

1. Cobalt sulphide membrane = 0.024 cm
2. Nickel sulphide membrane = 0.025 cm.

RESULTS AND DISCUSSION

Transport phenomena are often described by some extended form of the Nernst-Planck Flux equation [47]. Evaluation of flow requires integration of these equations under suitable boundary conditions. Sometime ago, based on the simple laws of electrolysis, Kittelburger [48] developed the following equation for the migration of ions through a barrier

$$dQ/dt = \frac{1}{Z_+ F R_m} \left[\frac{RT}{Z_+ F} \ln \frac{a_2}{a_1} - E_m \right] \left[\left(\frac{Z_-}{Z_+ + Z_-} \right) \left(\frac{E_m}{RT/Z_+ F \ln a_2/a_1} \right) + \left(\frac{Z_+}{Z_+ + Z_-} \right) \right] \quad [3]$$

where a_1 and a_2 are the activities of the two solutions of an electrolyte on either side of the membrane, Q is the number of milliequivalents of ions diffusing in time t seconds, E_m is the membrane concentration potential, R_m is the electrolyte resistance of the membrane in ohms, Z_+ , Z_- are the valency of cation and anion respectively, T is the absolute temperature, R is the gas const. and F is the Faraday const. Eq. [3] was used to give the rate dQ/dt at which various electrolysis diffuse through a membrane.

For electrolysis [1 :1], equation [3] simplifies to

$$\frac{dQ}{dt} = \frac{1}{2FR_m} [(E_c^+ - E_m)] \left[\frac{Em}{E_c^+} + 1 \right] \quad [4]$$

For [2: 1] electrolysis eq.[3] gives

$$\frac{dQ}{dt} = \frac{1}{3FR_m} \left[\left(\frac{E_c^+}{2} - Em \right) \right] \left[\left(\frac{Em}{E_c^+} + 1 \right) \right] \quad [5]$$

and for electrolytes of the type [3:1] it becomes.

$$\frac{dQ}{dt} = \frac{1}{4FR_m} \left[\left(\frac{E_c^+}{3} - Em \right) \right] \left[\left(\frac{Em}{E_c^+} + 1 \right) \right] \quad [6]$$

The values of membrane potential Em , membrane resistance R_m , and the diffusion rate dQ/dt derived from the experimental data and using eqs. [4-6] for both cobalt and nickel sulphide membranes in contact with different concentrations of various electrolytes are given in tables [1-30], and also depicted in Figs. 2-25 against the diffusion time while comparative values for various cations are shown in Figs. 26 and 27.

Tables 1-30 show that the membrane resistance R_m sequence for both the membranes at any given time for alkali metal ions is $Li^+ > Na^+ > K^+$; for alkaline earth metal ions is $Ba^{2+} > Ca^{2+} > Mg^{2+}$ and for aluminium it is highest. This sequence refers to the fact that there are very few coions in the membrane phase, and so in both the cases, the current carrying species are the cations. The charge on the ion has a very big effect on the mobility of the ions in the membranes. As the charge on the counter ions is increased, the membrane resistance increases. This may be ascribed to be due to the

Table 1
Values of Parameters For The Diffusion of KCl (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $10 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	E_{+c} (mV)	E_m (mV)	R_m (ohm)	$dQ/dt \times 10^7$ (millimol/S)
0.5	10.00	48.10	74.00	-54.60	665.60	-0.32
1.0	10.50	48.10	73.00	-54.00	665.60	-0.30
1.5	11.00	47.60	71.90	-53.40	658.00	-0.15
2.0	11.50	47.10	70.60	-52.80	639.00	-0.10
2.5	13.00	46.20	69.20	-50.90	609.00	-0.07
3.0	14.00	45.50	68.00	-49.90	567.00	-0.03
3.5	17.00	45.00	67.00	-47.00	524.00	0.05
4.0	19.00	45.00	66.00	-43.00	499.00	0.10

Vide Figs. 1,2,3,4.

Table 2
Values of Parameters For The Diffusion of KCl (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $15 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	E_{+c} (mV)	E_m (mV)	R_m (ohm)	$dQ/dt \times 10^7$ (millimol/S)
0.5	10.00	44.50	95.50	-59.10	570.40	2.60
1.0	11.00	44.00	94.20	-58.80	562.40	2.50
1.5	12.50	43.60	93.00	-55.80	534.70	2.70
2.0	13.00	43.40	91.80	-54.60	519.00	2.90
2.5	15.00	43.10	90.20	-51.90	519.00	3.40
3.0	17.00	43.00	88.50	-49.00	475.00	3.90
3.5	18.00	42.70	87.50	-48.70	441.30	4.00
4.0	19.00	42.50	86.50	-47.80	439.00	4.20

Vide Figs. 2, 3 and 4

Table 3
Values of Parameters For The Diffusion of KCl (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $20 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	E_{+c} (mV)	E_m (mV)	R_m (ohm)	$dQ/dt \times 10^7$ (millimol/S)
0.5	9.50	41.00	97.80	-66.60	376.70	3.10
1.0	10.00	40.80	96.50	-65.60	355.00	3.30
1.5	11.00	40.50	95.00	-64.20	354.00	3.40
2.0	12.00	40.00	94.50	-63.00	332.00	4.20
2.5	13.50	39.70	93.70	-60.40	328.50	4.40
3.0	14.00	39.30	92.30	-58.70	306.00	4.70
3.5	16.00	39.10	90.80	-57.90	286.00	5.00
4.0	18.00	39.00	89.50	-55.80	283.00	5.00

Vide Figs. 2, 3 and 4

Table 4
Values of Parameters For The Diffusion of KCl (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $25 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	E_{+c} (mV)	E_m (mV)	R_m (ohm)	$dQ/dt \times 10^7$ (millimol/S)
0.5	11.00	39.10	98.50	-67.60	282.40	3.31
1.0	11.50	39.00	97.00	-66.70	267.00	3.80
1.5	12.00	38.70	95.20	-65.70	259.00	3.70
2.0	13.00	38.30	94.00	-63.70	240.00	3.96
2.5	14.00	38.00	93.00	-63.30	242.00	3.98
3.0	16.00	37.70	92.50	-60.00	224.60	5.01
3.5	17.50	37.65	91.20	-57.05	218.00	5.80
4.0	19.00	37.50	90.00	-54.90	214.00	5.81

Vide Figs. 2, 3 and 4

Table 5
Values of Parameters For The Diffusion of NaCl (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $10 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E+c$ (mV)	E_m (mV)	R_m (ohm)	$dQ/dt \times 10^7$ (millimol/S)
0.5	11.00	18.50	85.00	-82.00	849.00	-0.63
1.0	12.50	18.00	83.80	-80.20	811.50	-0.55
1.5	13.00	17.70	82.40	-79.40	786.50	-0.42
2.0	15.00	17.40	81.00	-76.60	782.70	-0.37
2.5	17.00	17.00	79.70	-75.00	722.60	-0.33
3.0	17.50	16.70	78.30	-73.70	701.70	-0.24
3.5	18.50	16.50	77.00	-72.80	647.60	-0.15
4.0	20.00	16.40	76.00	-70.60	644.00	-0.13

Vide Figs. 5m 6 and 7

Table 6
Values of Parameters For The Diffusion of NaCl (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $15 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E+c$ (mV)	E_m (mV)	R_m (ohm)	$dQ/dt \times 10^7$ (millimol/S)
0.5	11.00	16.30	89.00	-86.50	765.60	-0.20
1.0	11.50	16.20	88.00	-85.50	710.00	-0.18
1.5	12.50	16.00	87.00	-84.00	699.00	0.10
2.0	14.00	15.70	86.00	-81.50	646.70	0.10
2.5	15.50	15.50	85.00	-79.40	627.00	0.20
3.0	17.00	15.10	83.80	-77.50	599.00	0.40
3.5	18.00	14.70	82.50	-76.70	576.60	0.50
4.0	19.00	14.50	81.30	-75.80	534.00	0.70

Vide Figs. 5m 6 and 7

Table 7
Values of Parameters For The Diffusion of NaCl (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $20 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	E_{+c} (mV)	E_m (mV)	R_m (ohm)	$dQ/dt \times 10^7$ (millimol/S)
0.5	10.00	14.10	97.00	-92.90	855.20	0.30
1.0	11.00	14.00	95.50	-90.10	560.40	0.40
1.5	12.00	13.50	94.20	-88.00	533.40	0.50
2.0	13.00	13.10	92.90	-87.50	499.00	0.70
2.5	14.00	13.00	91.30	-85.90	499.00	0.80
3.0	16.00	12.80	90.00	-83.60	462.60	0.90
3.5	17.00	12.50	89.00	-82.30	453.00	1.00
4.0	18.00	12.20	88.00	-80.90	417.10	1.20

Vide Figs. 5, 6 and 7

Table 8
Values of Parameters For The Diffusion of NaCl (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $25 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	E_{+c} (mV)	E_m (mV)	R_m (ohm)	$dQ/dt \times 10^7$ (millimol/S)
0.5	10.00	10.70	100.50	-97.50	539.00	0.40
1.0	11.00	10.30	99.20	-95.50	539.00	0.50
1.5	13.00	10.10	98.00	-92.30	499.00	0.60
2.0	14.00	10.00	96.80	-90.60	462.00	0.80
2.5	16.00	9.40	95.30	-87.80	443.40	1.00
3.0	19.00	9.20	94.20	-84.30	419.00	1.20
3.5	19.50	9.00	93.00	-83.40	399.00	1.30
4.0	20.00	8.80	92.00	-83.00	369.00	1.50

Vide Figs. 5, 6 and 7

Table 9
Values of Parameters For The Diffusion of LiCl (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $10 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E+c$ (mV)	E_m (mV)	R_m (ohm)	$dQ/dt \times 10^7$ (millimol/S)
0.5	10.00	14.90	89.00	-88.90	890.00	-0.89
1.0	10.80	14.40	88.00	-87.80	880.00	-0.79
1.5	12.50	14.00	87.00	-85.30	849.00	-0.79
2.0	14.00	13.50	86.00	-83.10	820.00	-0.63
2.5	17.00	13.00	85.00	-79.00	783.00	-0.44
3.0	18.00	12.60	83.80	-78.30	779.00	-0.30
3.5	19.00	12.20	82.50	-77.60	778.00	-0.29
4.0	20.00	12.00	81.30	-76.10	769.00	-0.25

Vide Figs. 8, 9 and 10

Table 10
Values of Parameters For The Diffusion of LiCl (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $15 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E+c$ (mV)	E_m (mV)	R_m (ohm)	$dQ/dt \times 10^7$ (millimol/S)
0.5	9.00	12.30	99.00	-95.80	839.00	-0.61
1.0	12.00	12.00	97.00	-89.70	832.00	-0.57
1.5	14.00	11.50	95.20	-86.80	772.30	-0.41
2.0	15.00	11.10	94.00	-85.50	765.60	-0.15
2.5	15.50	10.70	93.00	-85.30	759.00	-0.09
3.0	17.00	10.40	92.00	-83.30	749.00	0.10
3.5	19.00	10.00	91.20	-81.50	754.00	0.20
4.0	21.00	9.50	90.00	-79.10	749.00	0.30

Vide Figs. 8, 9 and 10

Table 11
Values of Parameters For The Diffusion of LiCl (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $20 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E+C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	9.50	104.00	-98.10	754.50	-0.54
1.0	12.00	9.10	102.80	-91.00	741.20	-0.43
1.5	13.00	8.80	101.30	-89.00	732.30	-0.11
2.0	14.00	8.70	100.00	-86.70	696.60	0.10
2.5	15.50	8.40	98.70	-86.40	950.10	0.10
3.0	16.50	8.00	97.00	-86.30	615.20	0.40
3.5	18.00	7.70	95.50	-86.00	580.00	0.50
4.0	19.00	7.50	94.00	-84.50	569.00	1.10

Vide Figs. 8, 9 and 10

Table 12
Values of Parameters For The Diffusion of LiCl (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $25 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E+C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	12.50	6.70	109.00	-100.00	665.60	-0.42
1.0	14.00	6.50	108.00	-98.30	646.00	-0.36
1.5	15.50	6.10	107.00	-97.50	609.00	0.00
2.0	17.00	5.70	106.20	-96.10	569.00	0.30
2.5	17.50	5.00	105.00	-94.50	530.00	0.70
3.0	18.00	4.60	103.70	-93.10	519.00	1.20
3.5	18.50	4.50	102.20	-91.40	509.00	1.30
4.0	20.00	4.20	101.00	-90.60	509.00	1.50

Vide Figs. 8, 9 and 10

Table 13
Values of Parameters For The Diffusion of CaCl_2 (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $10 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E+C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	10.00	3.80	90.50	-87.70	614.30	-0.53
1.0	12.00	3.50	89.50	-85.20	609.00	-0.43
1.5	13.50	3.10	88.50	-83.40	580.80	-0.32
2.0	15.50	2.80	87.50	-80.30	595.70	-0.25
2.5	17.00	2.40	86.50	-79.00	564.50	-0.12
3.0	18.50	1.90	85.30	-77.80	563.40	-0.10
3.5	21.00	1.50	84.00	-75.40	556.00	0.00
4.0	22.00	1.10	82.80	-75.30	549.00	0.00

Vide 11, 12 and 13

Table 14
Values of Parameters For The Diffusion of CaCl_2 (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $15 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E+C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	1.00	100.50	-93.00	516.20	-0.28
1.0	13.50	0.50	98.50	-89.60	511.70	-0.15
1.5	16.00	0.10	96.70	-86.00	499.00	-0.14
2.0	17.00	-0.50	95.50	-85.40	464.00	-0.09
2.5	18.00	-0.80	94.50	-84.70	457.80	-0.08
3.0	19.00	-1.20	93.50	-83.80	462.00	-0.08
3.5	21.00	-1.70	92.70	-82.10	456.00	0.10
4.0	22.00	-2.00	91.50	-81.80	461.00	0.20

Vide Figs. 11, 12 and 13

Table 15
Values of Parameters For The Diffusion of CaCl_2 (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $20 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E+c$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	-2.50	105.50	-98.20	399.00	-0.19
1.0	11.50	-3.00	104.30	-98.10	385.00	-0.09
1.5	13.00	-3.50	102.80	-96.30	374.00	-0.05
2.0	15.00	-3.90	101.50	-93.20	361.00	0.20
2.5	17.00	-4.30	100.20	-90.70	344.50	0.30
3.0	18.50	-4.80	98.50	-89.40	341.30	0.30
3.5	19.00	-5.00	97.50	-89.10	349.00	0.30
4.0	19.00	-5.20	97.50	-89.00	349.00	0.30

Vide Figs. 11, 12 and 13

Table 16
Values of Parameters For The Diffusion of CaCl_2 (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $25 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E+c$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.00	-4.10	110.50	-101.50	283.80	0.40
1.0	12.00	-4.50	109.50	-100.70	274.00	0.60
1.5	13.00	-5.00	108.50	-99.40	271.10	0.60
2.0	15.00	-5.50	107.70	-96.40	259.00	1.00
2.5	16.50	-6.00	106.50	-94.50	253.00	1.30
3.0	18.00	-6.50	105.20	-93.20	244.10	1.70
3.5	19.00	-7.00	103.70	-92.40	240.00	2.10
4.0	20.00	-7.30	102.50	-91.70	239.00	2.20

Vide Figs. 11, 12 and 13

Table 17
Values of Parameters For The Diffusion of BaCl₂ (0.1M/0.001M) Through
Cobalt Sulphide Membrane at 10±0.1°C

Time (hr)	Conc. (C ₁) (M) x 10 ⁴	E _{obs} (mV)	E _{+c} (mV)	E _m (mV)	R _m (ohm)	dQ/dt x10 ⁷ (millimol/ S)
0.5	9.50	0.50	93.50	-92.10	429.00	-0.83
1.0	10.50	0.10	92.30	-90.30	424.00	-0.81
1.5	12.50	1.70	91.50	-86.80	424.00	-0.51
2.0	13.50	1.10	90.50	-86.30	431.00	-0.50
2.5	15.00	0.20	89.50	-85.30	422.40	-0.49
3.0	17.00	-0.50	88.30	-82.80	421.60	-0.37
3.5	18.50	-0.80	87.00	-81.40	415.60	-0.33
4.0	20.00	-1.00	85.80	-79.90	415.00	-0.17

Vide Fig. 14, 15 and 16

Table 18
Values of Parameters For The Diffusion of BaCl₂ (0.1M/0.001M) Through
Cobalt Sulphide Membrane at 15±0.1°C

Time (hr)	Conc. (C ₁) (M) x 10 ⁴	E _{obs} (mV)	E _{+c} (mV)	E _m (mV)	R _m (ohm)	dQ/dt x10 ⁷ (millimol/ S)
0.5	10.00	-1.70	102.00	-96.30	339.00	-0.31
1.0	10.50	-2.00	101.00	-96.00	332.30	-0.24
1.5	12.00	-2.70	99.20	-94.50	339.00	-0.24
2.0	14.00	-3.00	98.00	-91.40	331.00	-0.07
2.5	14.50	-3.70	97.00	-90.90	330.00	-0.02
3.0	16.00	-4.20	96.00	-89.70	329.00	0.00
3.5	18.00	-4.80	94.20	-87.40	326.00	0.10
4.0	19.00	-5.00	93.00	-86.50	326.00	0.20

Vide Fig. 14, 15 and 16

Table 19
Values of Parameters For The Diffusion of BaCl₂ (0.1M/0.001M) Through
Cobalt Sulphide Membrane at 20±0.1°C

Time (hr)	Conc. (C ₁) (M) x 10 ⁴	E _{obs} (mV)	E _{+c} (mV)	E _m (mV)	R _m (ohm)	dQ/dt x10 ⁷ (millimol/ S)
0.5	10.00	-5.00	108.40	-101.30	289.60	0.10
1.0	11.00	-5.50	107.40	-100.00	286.60	0.10
1.5	11.50	-5.80	105.50	-99.70	289.00	0.20
2.0	12.50	-6.00	104.50	-98.20	288.00	0.30
2.5	14.00	-6.50	103.00	-96.40	287.00	0.40
3.0	15.00	-6.90	101.40	-95.10	287.00	0.40
3.5	16.50	-7.10	100.00	-94.30	286.00	0.60
4.0	17.00	-7.50	98.50	-93.30	204.00	0.80

Vide Figs.14, 15 and 16

Table 20
Values of Parameters For The Diffusion of BaCl₂ (0.1M/0.001M) Through
Cobalt Sulphide Membrane at 25±0.1°C

Time (hr)	Conc. (C ₁) (M) x 10 ⁴	E _{obs} (mV)	E _{+c} (mV)	E _m (mV)	R _m (ohm)	dQ/dt x10 ⁷ (millimol/ S)
0.5	9.50	-8.10	113.50	-107.80	274.00	0.20
1.0	10.00	-8.70	112.50	-106.60	266.00	0.30
1.5	10.50	-9.00	111.50	-106.00	274.00	0.40
2.0	11.50	-10.60	110.70	-105.30	264.60	0.40
2.5	13.00	-10.00	109.50	-103.20	266.00	0.50
3.0	15.00	-10.50	108.20	-100.20	268.00	0.60
3.5	16.00	-11.00	106.70	-99.50	263.70	0.80
4.0	18.00	-11.80	105.50	-97.40	259.70	0.90

Vide Figs. 14, 15 and 16

Table 21
Values of Parameters For The Diffusion of MaCl_2 (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $10 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E+C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	10.50	9.45	54.10	-58.50	459.00	-0.42
1.0	12.00	9.10	52.60	-56.10	429.00	-0.29
1.5	14.00	8.75	51.00	-53.00	427.00	-0.13
2.0	15.50	8.20	49.80	-51.30	349.00	-0.01
2.5	16.50	7.70	48.40	-48.00	275.00	0.40
3.0	18.50	7.35	46.90	-47.30	270.00	0.50
3.5	19.50	7.10	45.40	-46.80	270.00	0.50
4.0	20.50	7.00	44.00	-46.40	259.70	0.60

Vide Figs. 17, 18 and 19

Table 22
Values of Parameters For The Diffusion of MaCl_2 (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $15 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E+C$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	10.00	6.55	59.10	-63.40	366.20	-0.02
1.0	11.50	6.15	57.60	-62.80	349.00	0.00
1.5	12.50	5.50	56.00	-60.80	345.70	0.30
2.0	15.50	5.00	54.80	-57.70	335.70	0.40
2.5	17.00	4.50	53.40	-55.80	309.30	0.60
3.0	18.00	3.70	51.90	-53.00	257.00	0.80
3.5	18.00	3.10	50.40	-52.30	253.50	0.80
4.0	19.00	3.00	49.00	-52.30	238.50	0.90

Vide Figs. 17, 18 and 19

Table 23
Values of Parameters For The Diffusion of MaCl_2 (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $20 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	E_{+c} (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	11.50	4.75	63.30	-65.00	309.80	0.30
1.0	13.00	4.50	61.80	-62.50	299.00	0.50
1.5	14.50	4.20	60.30	-61.10	289.00	0.50
2.0	16.00	4.00	58.80	-57.20	276.70	0.60
2.5	18.00	3.50	57.40	-55.40	210.20	0.70
3.0	19.00	3.10	55.90	-54.60	199.00	1.20
3.5	20.00	2.80	54.40	-53.70	169.00	1.20
4.0	20.00	2.70	53.00	-53.60	169.00	1.50

Vide Figs. 17, 18 and 19

Table 24
Values of Parameters For The Diffusion of MaCl_2 (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $25 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	E_{+c} (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	10.00	2.00	67.30	-70.30	265.60	0.40
1.0	11.50	1.75	65.80	-67.60	243.40	0.60
1.5	12.50	1.45	64.30	-66.10	239.00	0.70
2.0	14.00	1.10	62.80	-64.20	237.40	0.80
2.5	15.50	0.80	61.40	-62.10	199.00	1.20
3.0	16.50	0.30	59.90	-61.40	189.00	1.30
3.5	17.00	0.00	57.40	-60.10	179.00	2.20
4.0	18.00	-0.50	57.00	-60.40	152.00	2.30

Vide Figs. 17, 18 and 19

Table 25
Values of Parameters For The Diffusion of AlCl_3 (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $10 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E+c$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	9.50	-17.20	84.00	-99.00	499.00	-0.40
1.0	10.50	-18.60	82.80	-98.70	499.00	0.00
1.5	12.50	-20.80	81.40	-97.00	494.00	0.20
2.0	13.50	-20.50	80.40	-95.00	489.00	0.50
2.5	15.00	-21.30	80.00	-93.50	487.00	1.00
3.0	17.00	-21.00	78.70	-91.00	479.00	1.30
3.5	18.50	-20.60	76.00	-90.00	475.20	1.70
4.0	20.00	-21.40	75.00	-88.00	469.00	1.80

Vide Figs. 20, 21 and 22

Table 26
Values of Parameters For The Diffusion of AlCl_3 (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $15 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	$E+c$ (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	10.00	-18.20	88.00	-101.50	459.00	0.30
1.0	10.50	-18.50	87.00	-100.00	458.00	0.90
1.5	12.00	-20.30	86.00	-99.00	457.00	1.10
2.0	14.00	-21.30	85.00	-96.50	450.00	1.50
2.5	14.50	-20.30	84.00	-94.00	449.00	1.50
3.0	16.00	-18.60	82.80	-91.50	439.50	2.20
3.5	18.00	-19.00	81.50	-90.00	434.40	2.10
4.0	19.00	-20.00	80.30	-89.00	431.00	3.90

Vide Figs. 20, 21 and 22

Table 27
Values of Parameters For The Diffusion of AlCl_3 (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $20 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	E_{+c} (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	10.00	-20.40	96.00	-105.10	439.00	3.00
1.0	11.00	-21.20	94.50	-103.00	434.80	3.40
1.5	11.50	-20.60	93.20	-101.20	433.50	3.80
2.0	12.50	-21.10	91.90	-100.00	430.50	4.30
2.5	14.00	-22.00	90.30	-98.50	411.20	4.50
3.0	15.00	-22.00	89.00	-97.00	408.00	5.00
3.5	16.50	-22.90	88.00	-96.00	404.20	5.50
4.0	17.00	-23.00	87.00	-95.50	389.00	5.80

Vide Figs. 20, 21 and 22

Table 28
Values of Parameters For The Diffusion of AlCl_3 (0.1M/0.001M) Through
Cobalt Sulphide Membrane at $25 \pm 0.1^\circ\text{C}$

Time (hr)	Conc. (C_1) (M) $\times 10^4$	E_{obs} (mV)	E_{+c} (mV)	E_m (mV)	R_m (ohm)	dQ/dt $\times 10^7$ (millimol/ S)
0.5	9.50	-26.10	101.50	-112.20	399.00	4.40
1.0	10.00	-26.50	100.20	-110.50	390.70	4.50
1.5	10.50	-24.50	99.00	-107.50	389.00	4.80
2.0	11.50	-22.40	97.80	-105.00	376.40	5.60
2.5	13.00	-25.00	96.30	-103.50	359.00	5.50
3.0	15.00	-26.30	95.20	-102.00	357.00	6.60
3.5	16.00	-29.60	94.00	-100.50	341.00	8.00
4.0	18.00	-29.80	93.00	-99.00	299.00	8.50

Vide Figs. 20, 21 and 22

Table 29
Values of Parameters For The Diffusion of monovalent, divalent and trivalent electrolytes at The end of 1/2 and 4 hour periods Through Cobalt Sulphide Membrane at $25 \pm 0.1^\circ\text{C}$

Parameters Electrolyte	E_{obs} (mV)		E_{+c} (mV)		E_m (mV)		R_m (ohm)		$dQ/dtx10^7$ (millimol/s)	
	$\frac{1}{2}$ h	4 h	$\frac{1}{2}$ h	4 h	$\frac{1}{2}$ h	4 h	$\frac{1}{2}$ h	4 h	$\frac{1}{2}$ h	4 h
KCl	39.10	37.50	98.50	90.00	-69.60	-54.90	282.40	214.00	3.30	5.80
NaCl	10.70	8.80	100.50	92.00	-99.50	-83.00	539.00	369.00	0.40	1.70
LiCl	6.70	4.20	109.00	101.00	-100.40	-90.60	665.60	499.00	-0.40	1.50
CaCl_2	-4.10	-7.30	110.50	102.50	-101.50	-91.70	283.80	239.00	0.40	2.20
BaCl_2	-8.10	-11.80	113.50	105.50	-107.80	-97.40	274.00	259.70	0.20	0.90
NgCl_2	2.00	-0.50	67.30	57.00	-70.30	-60.40	265.60	152.00	0.40	2.30
AlCl_3	-26.10	-29.80	99.50	91.00	-112.20	-99.00	399.00	299.00	-0.50	-0.10

Table 30
Values of Parameters For The Diffusion of monovalent, divalent and trivalent electrolytes at The end of 1/2 and 4 hour periods Through nickel Sulphide Membrane at $25 \pm 0.1^\circ\text{C}$

Parameters Electrolyte	E_{obs} (mV)		E_{+c} (mV)		E_m (mV)		R_m (ohm)		$dQ/dtx10^7$ (millimol/s)	
	$\frac{1}{2}$ h	4 h	$\frac{1}{2}$ h	4 h	$\frac{1}{2}$ h	4 h	$\frac{1}{2}$ h	4 h	$\frac{1}{2}$ h	4 h
KCl	43.10	41.00	97.00	90.00	-63.40	-50.40	260.50	109.00	5.40	10.10
NaCl	14.70	12.00	98.50	96.00	-93.50	-79.20	425.00	284.20	0.30	3.10
LiCl	9.50	7.30	107.00	99.00	-97.00	-87.00	474.50	341.20	1.10	3.00
CaCl_2	-5.00	-6.00	109.00	102.00	-100.30	-90.40	264.00	204.24	0.60	1.90
BaCl_2	-7.50	-7.30	110.50	102.50	-105.20	-93.40	259.00	234.00	0.00	0.90
NgCl_2	4.70	2.50	65.20	54.00	-67.00	-57.40	217.00	139.00	1.10	3.00
AlCl_3	-25.10	-24.00	98.00	89.50	-109.20	-96.00	381.20	339.80	-0.40	-0.20

Vide Figs. 23-25

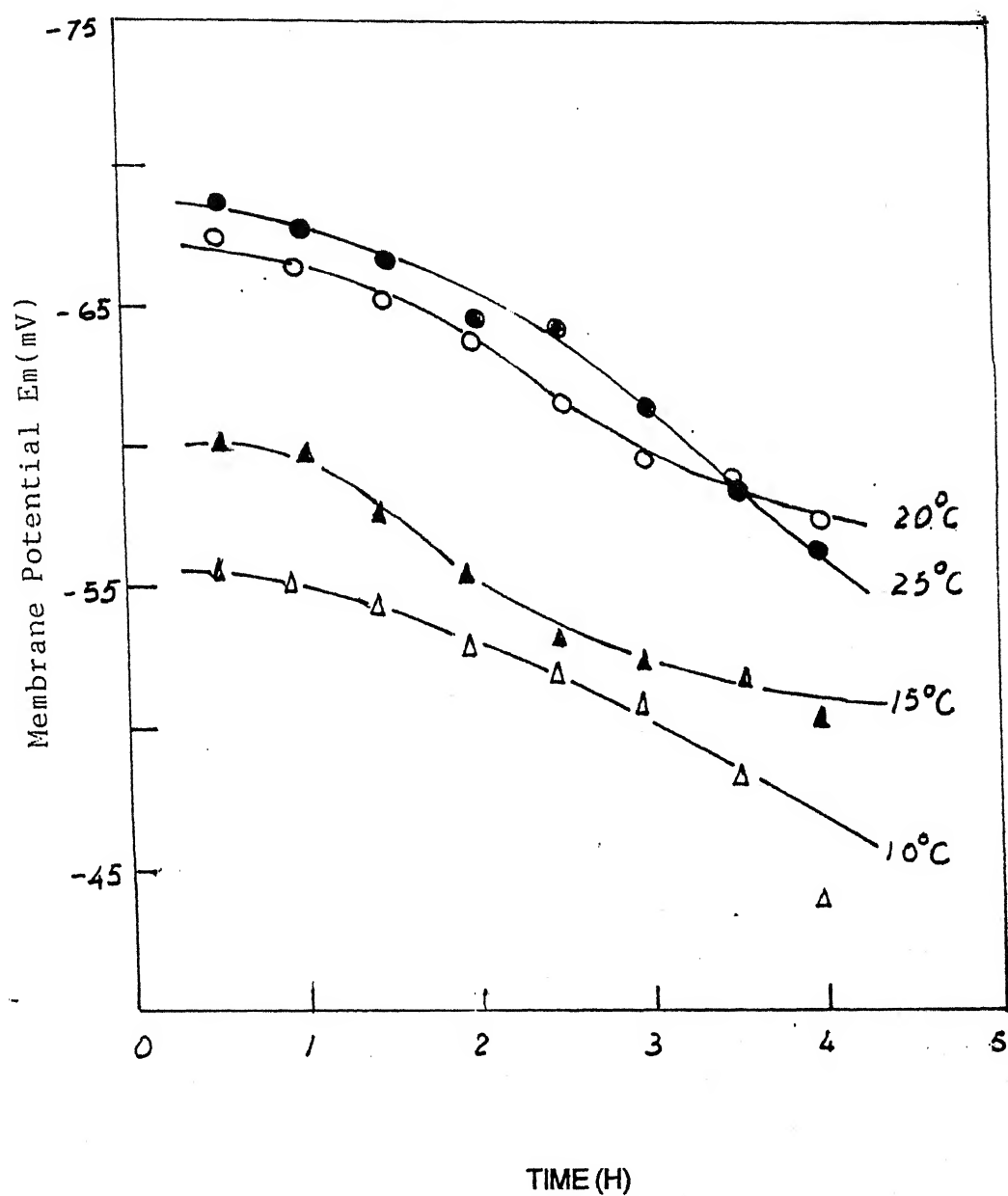


FIG. 2

Plots of membrane potential E_m (mV) against Time (h) at different temperature across cobalt sulphide membrane using KCl electrolyte

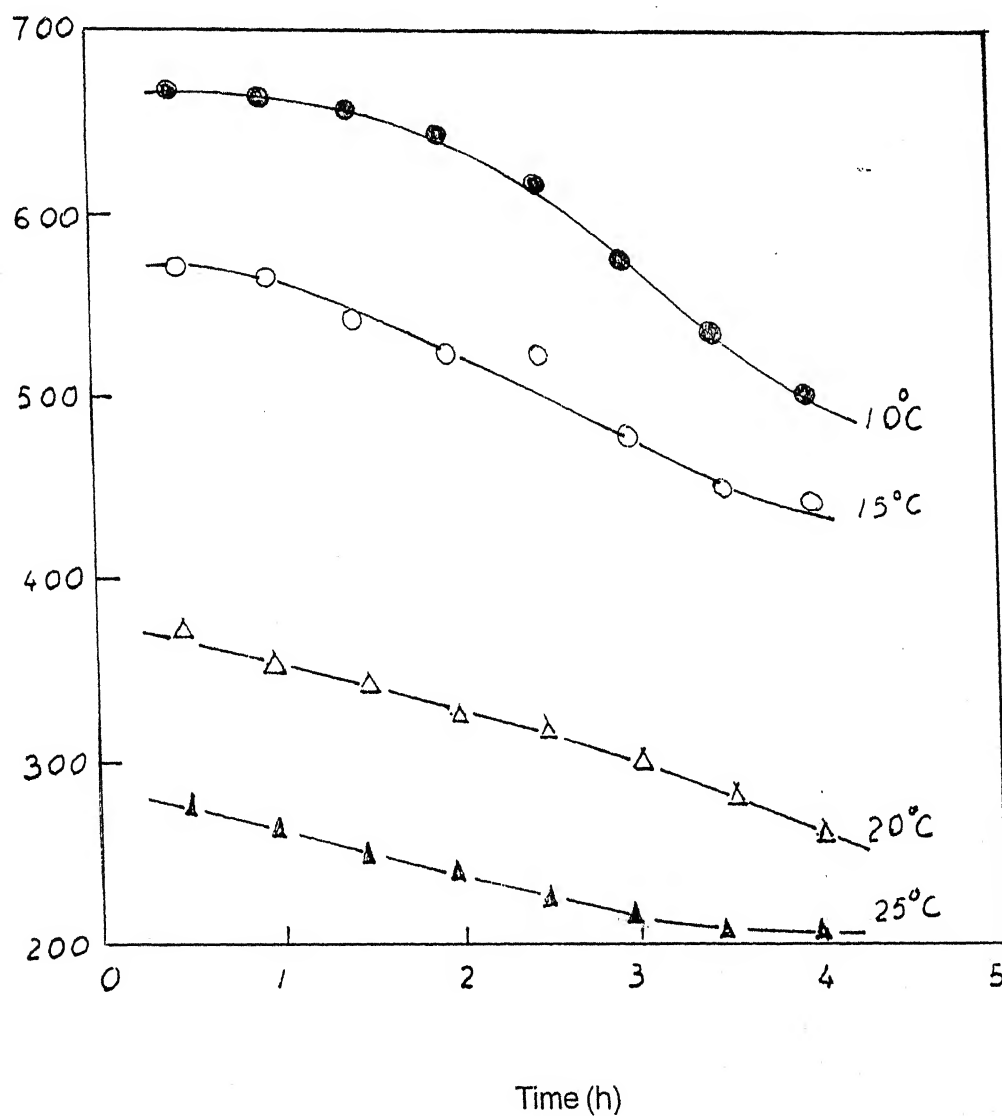


FIG. - 3

Plots of membrane resistance R_m (ohm) against Time (h) at different temperatures across cobalt phosphate-membrane using KCl electrolyte.

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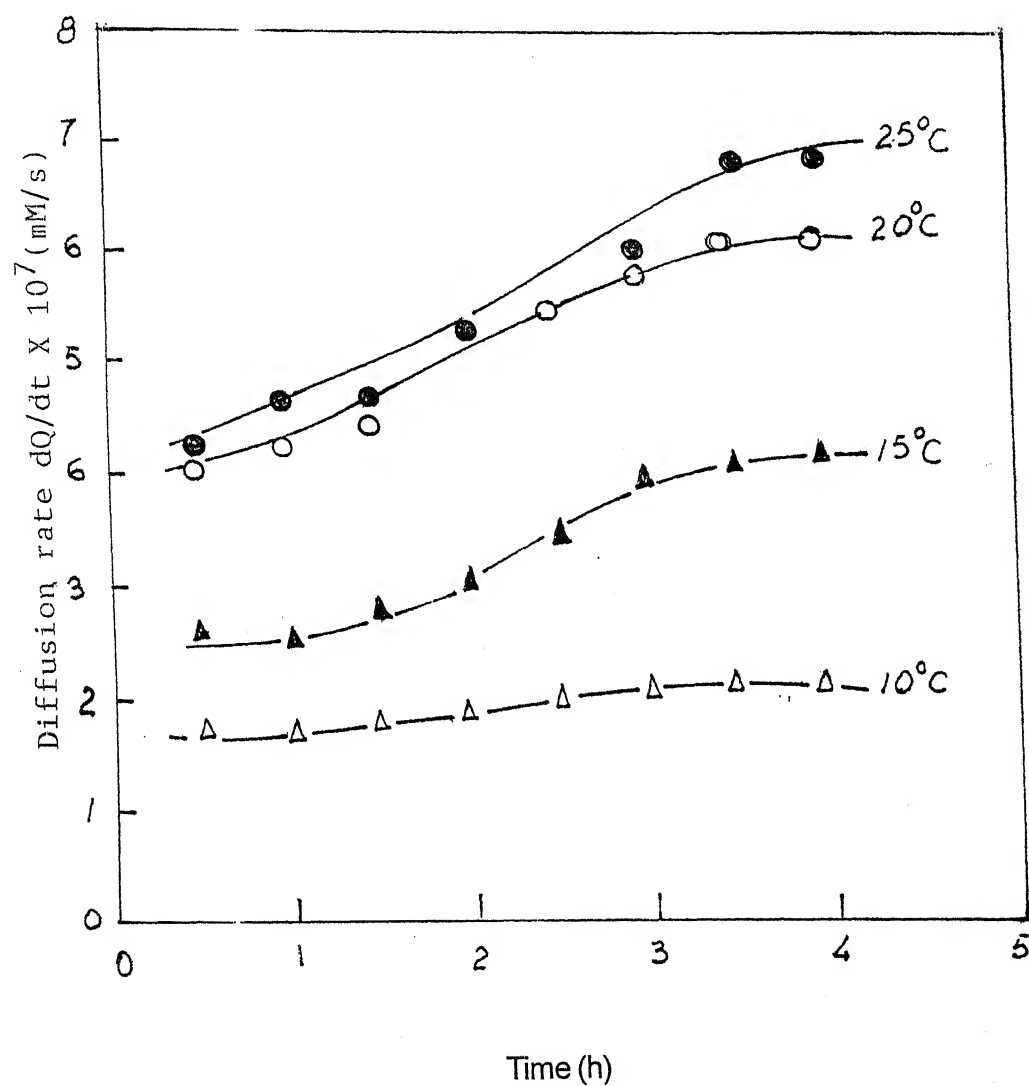


Fig. - 4

PLOTS OF DIFFUSION RATE dQ/dt (mM/s) AGAINST TIME (h)
AT DIFFERENT TEMPERATURES ACROSS COBALT SULPHIDE
MEMBRANE USING KCl ELECTROLYTE.

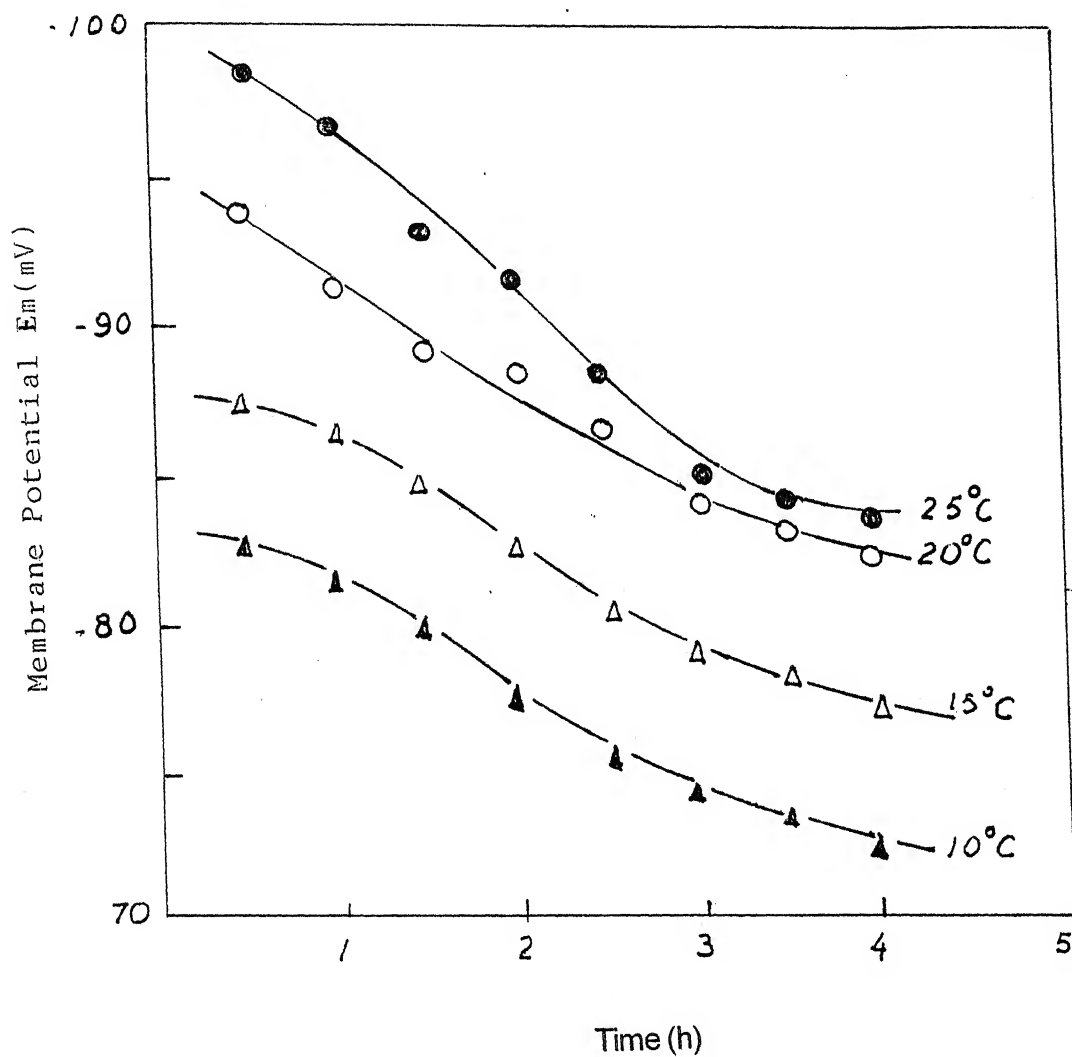


Fig. - 5

PLOTS OF DIFFUSION RATE dQ/dt (mM/s) AGAINST TIME (h)
AT DIFFERENT TEMPERATURES ACROSS COBALT SULPHIDE
MEMBRANE USING NaCl ELECTROLYTE.

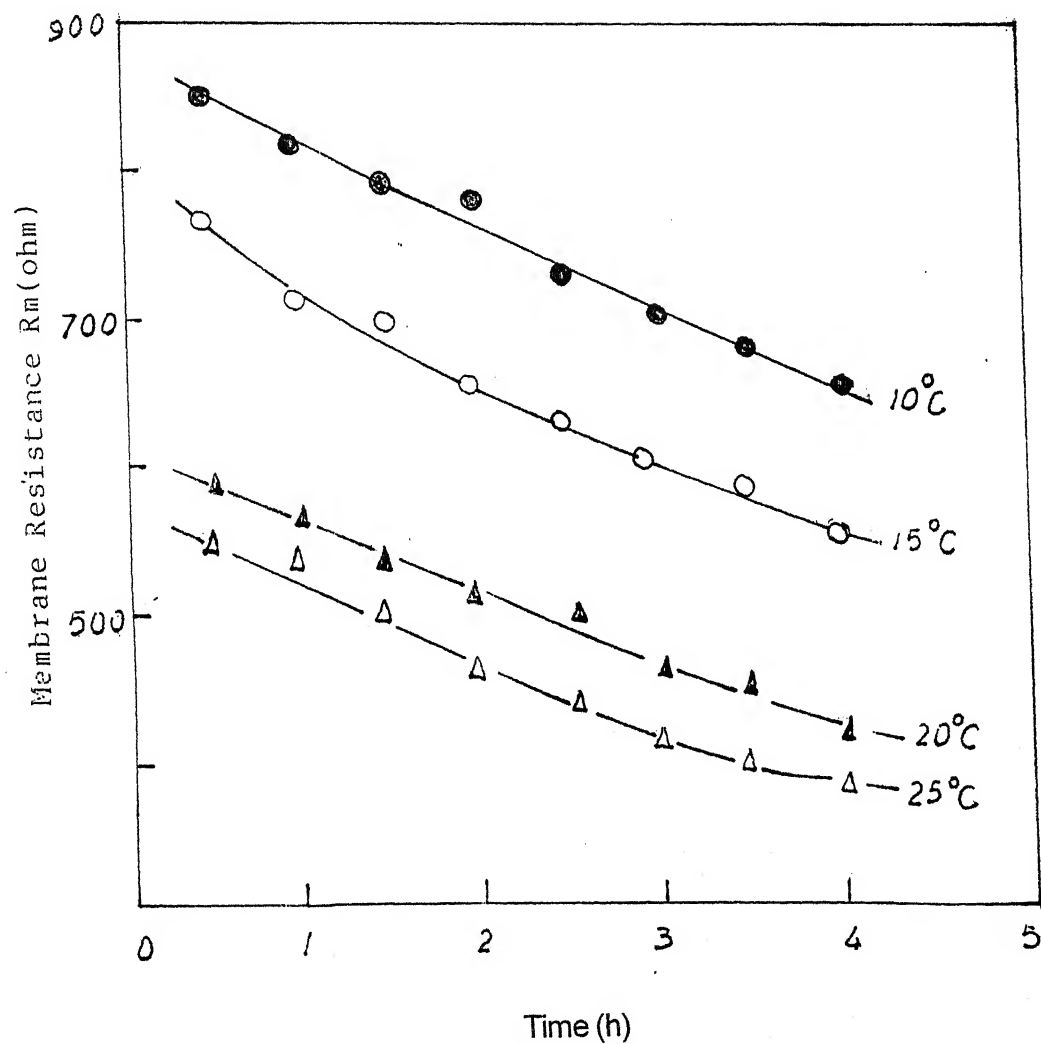


Fig. - 6

PLOTS OF MEMBRANE RESISTANCE R_m (ohm) AGAINST TIME (h) AT DIFFERENT TEMPERATURES ACROSS COBALT SULPHIDE MEMBRANE USING NaCl ELECTROLYTE.

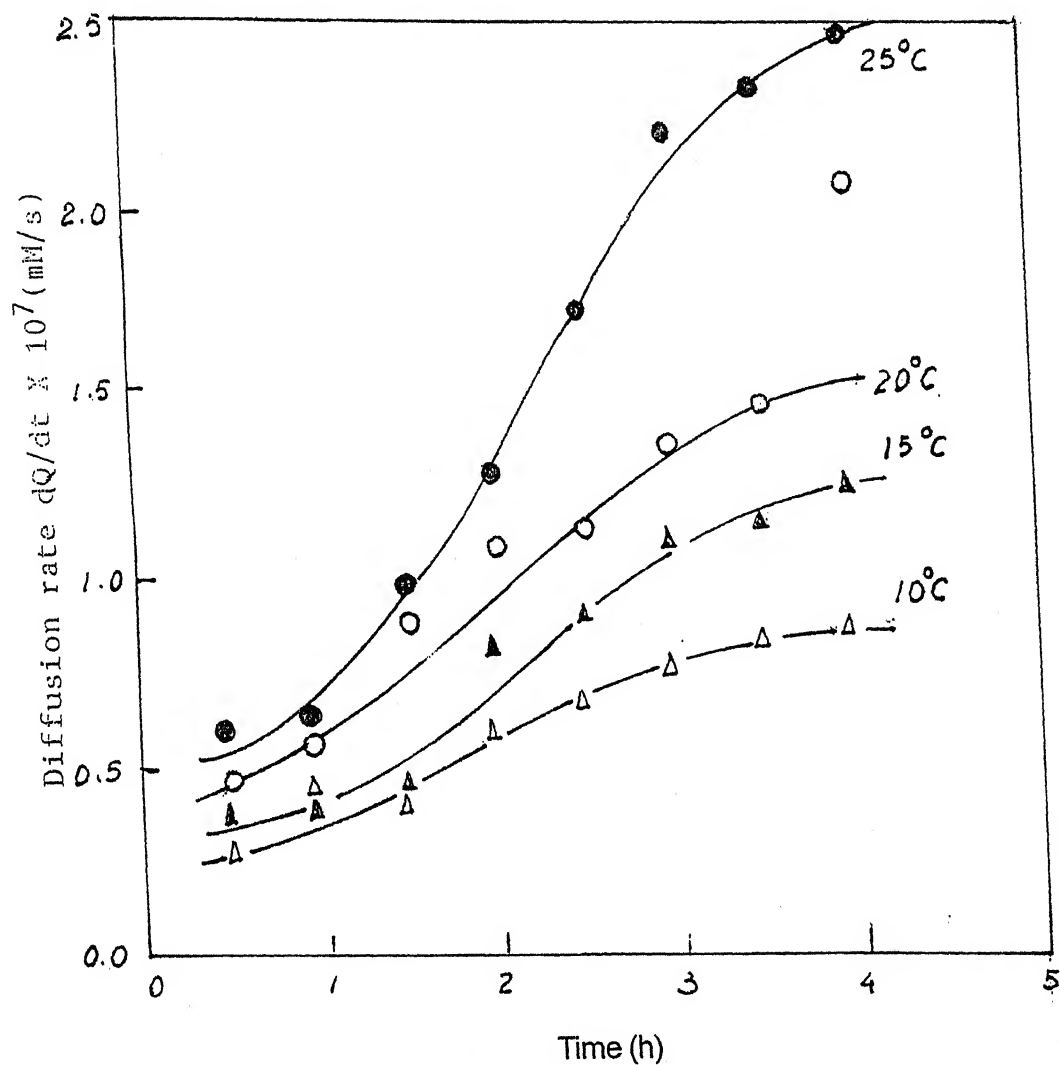


Fig. - 7

PLOTS OF DIFFUSION RATE dQ/dt (mM/s) AGAINST TIME (h)
AT DIFFERENT TEMPERATURES ACROSS COBALT
SULPHIDE MEMBRANE USING NaCl ELECTROLYTE.

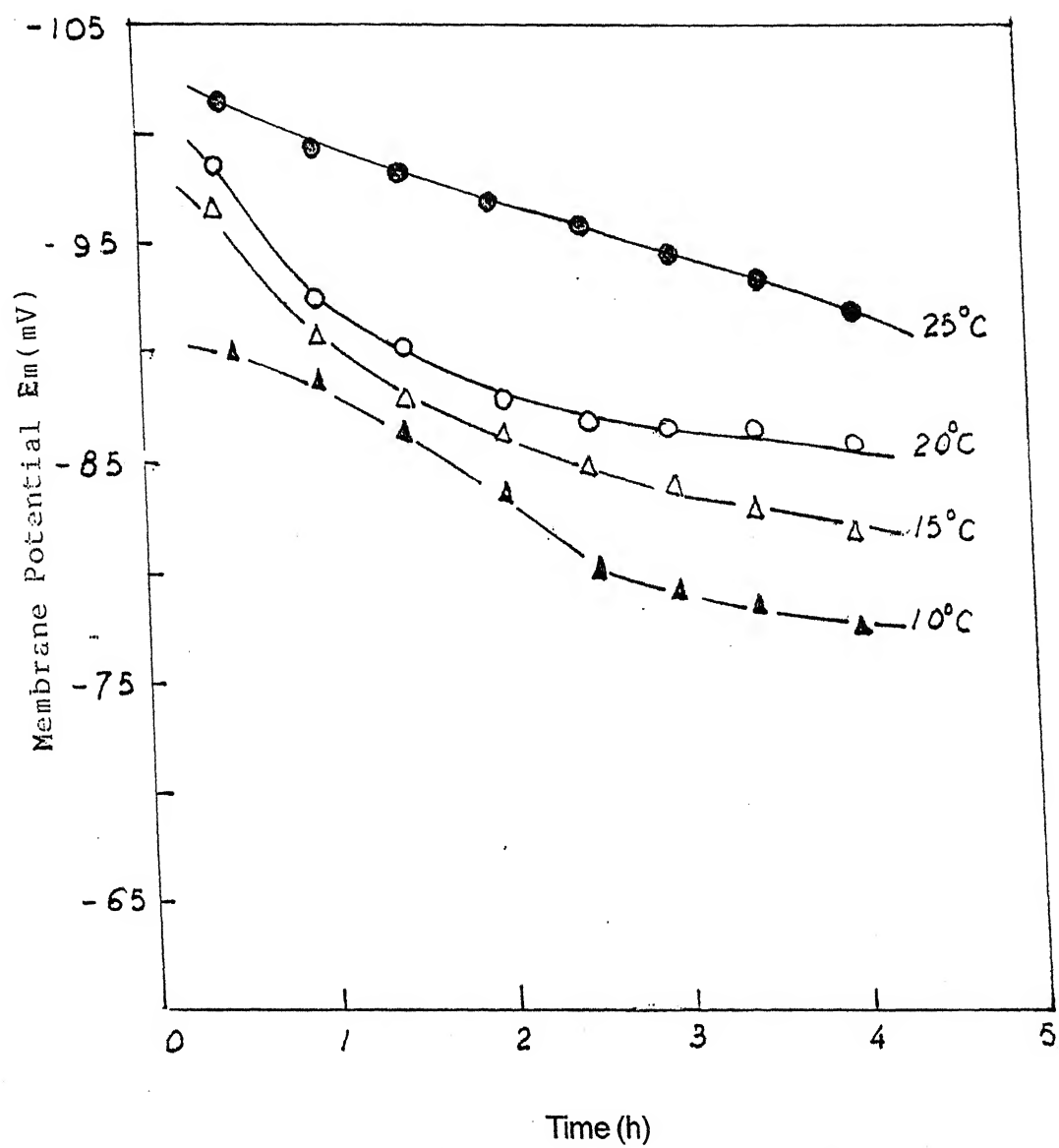


Fig. - 8

PLOTS OF MEMBRANE POTENTIAL E_m (mV) AGAINST TIME (h)
AT DIFFERENT TEMPERATURES ACROSS COBALT SULPHIDE
MEMBRANE USING LiCl ELECTROLYTE

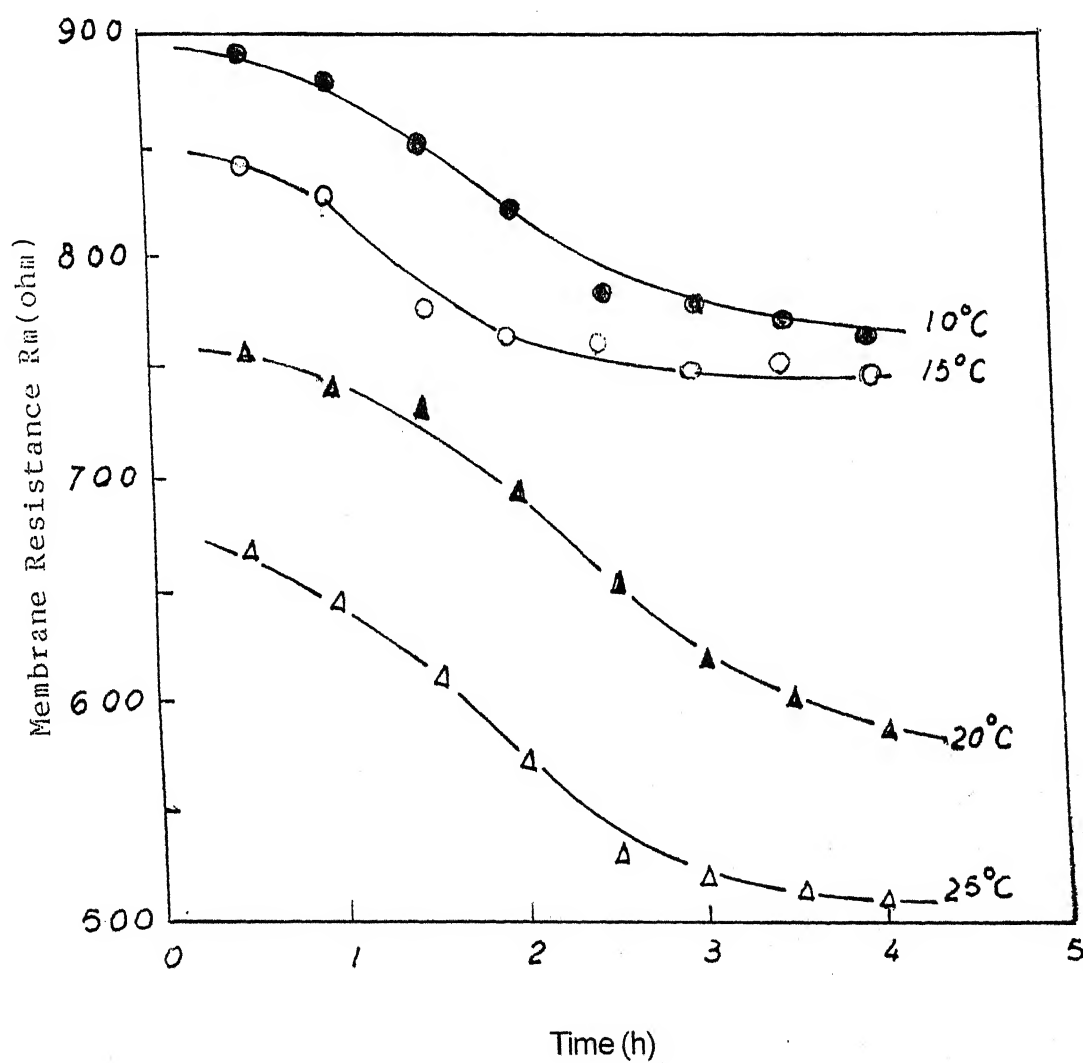


FIG. - 9

PLOTS OF MEMBRANE RESISTANCE R_m (ohm) AGAINST TIME (h)
AT DIFFERENT TEMPERATURE ACROSS COBALT SULPHIDE MEMBRANE
USING LiCl ELECTROLYTE.

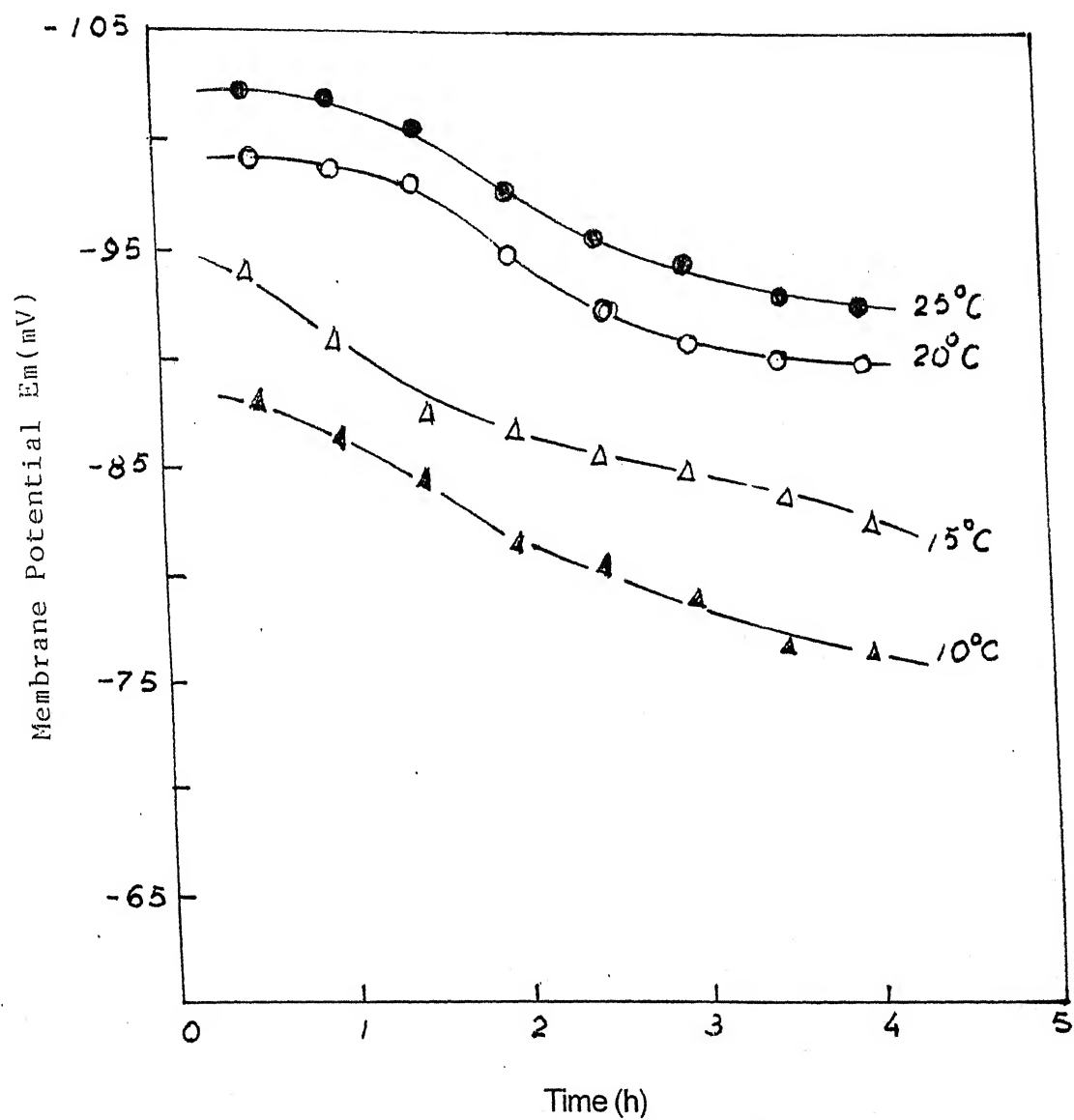


FIG. - 11

Plots of membrane potential E_m (mV) against Time (h) at different temperatures across cobalt sulphide membrane using CaCl_2 electrolyte.

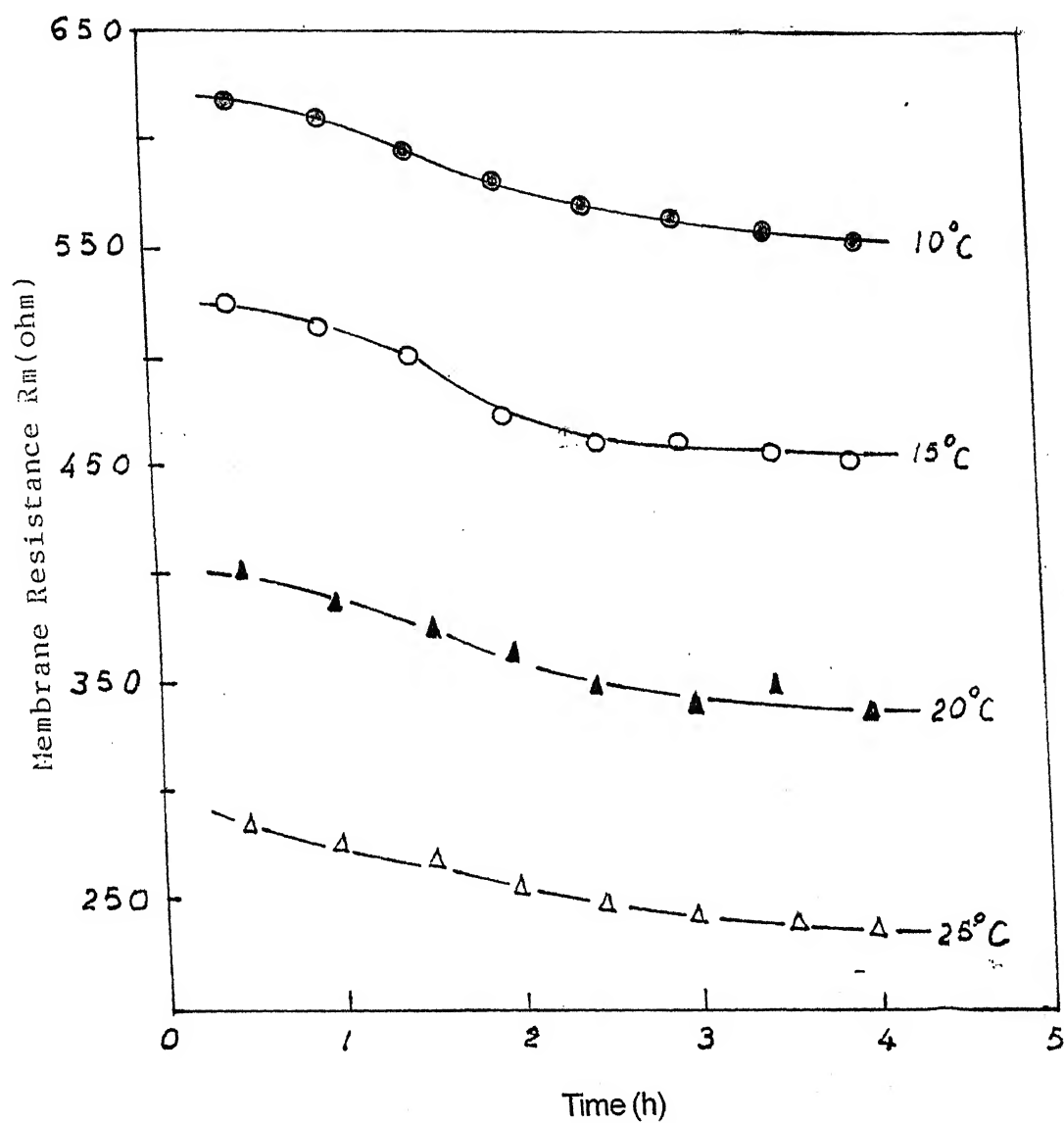


FIG. - 12

Plots of membrane resistance R_m (ohm) against Time (h) at different temperatures across cobalt sulphide membrane using CaCl_2 Electrolyte.

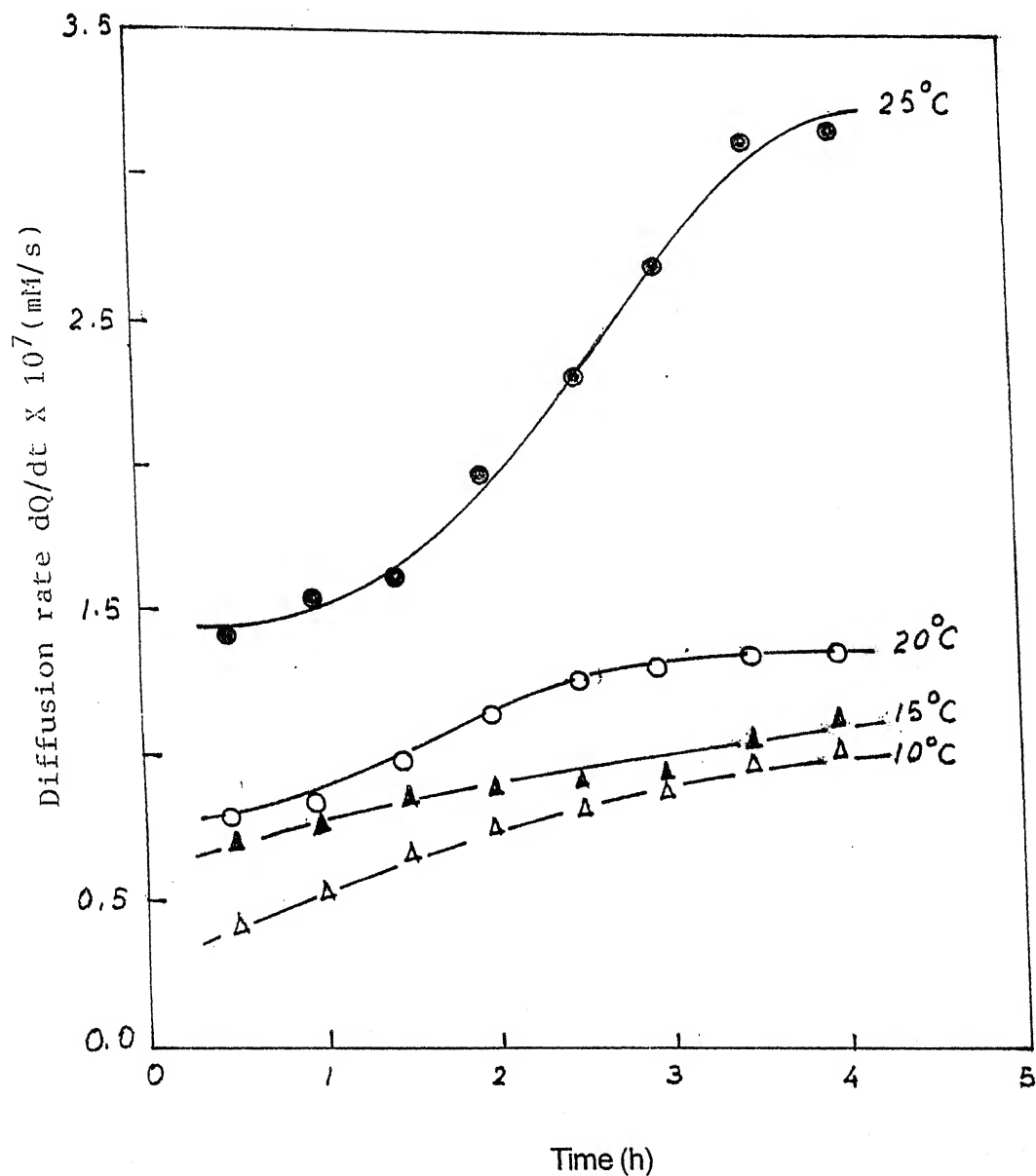


FIG. - 13

Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperatures across cobalt sulphide membrane using CaCl_2 electrolyte

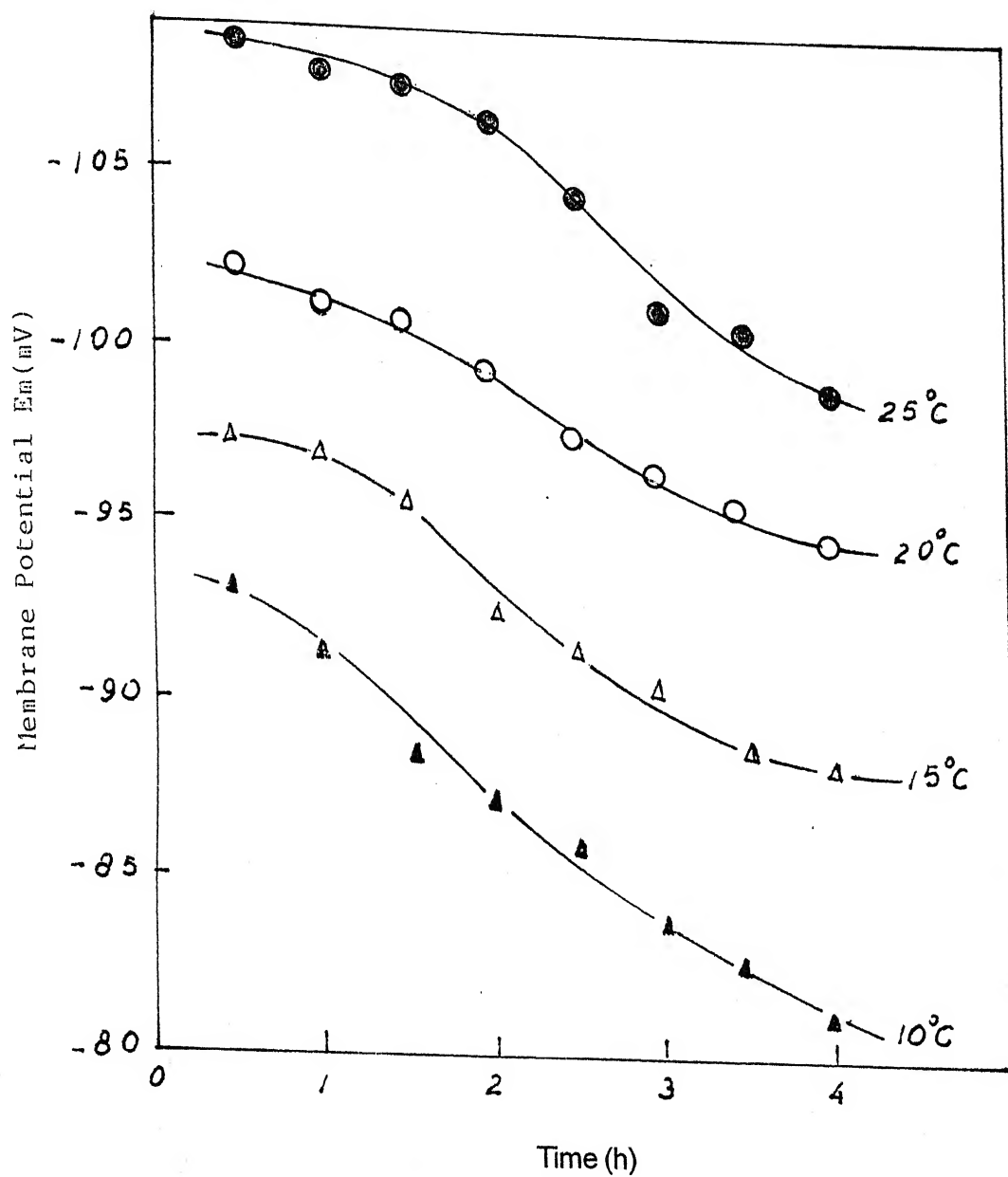


FIG. - 14

Plots of membrane potential E_m (mV) against Time (h) at different temperatures across cobalt sulphide membrane using BaCl_2 electrolyte.

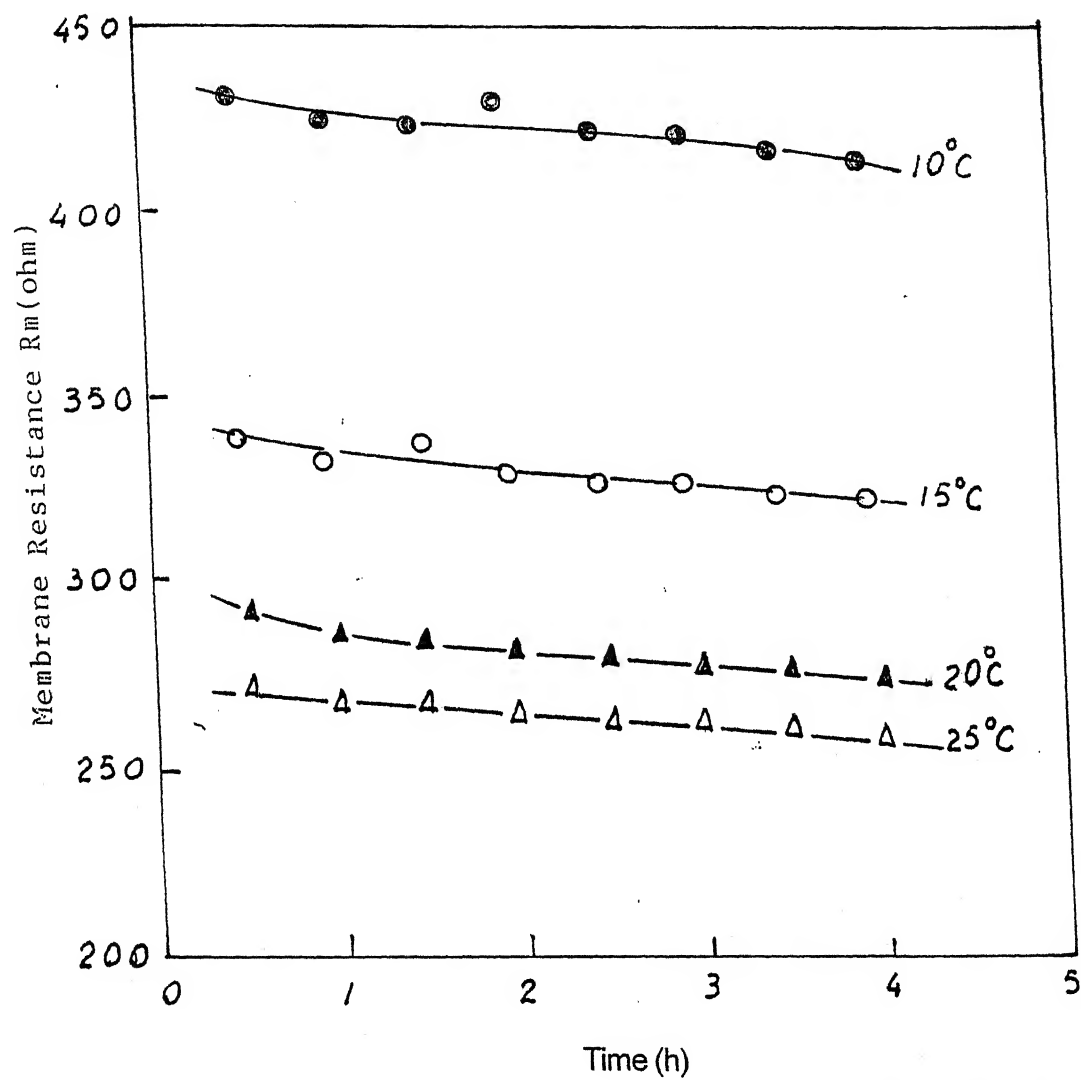


FIG. - 15

Plots of membrane resistance R_m (ohm) against Time (h) at different temperature across cobalt sulphide membrane using $BaCl_2$ electrolyte.

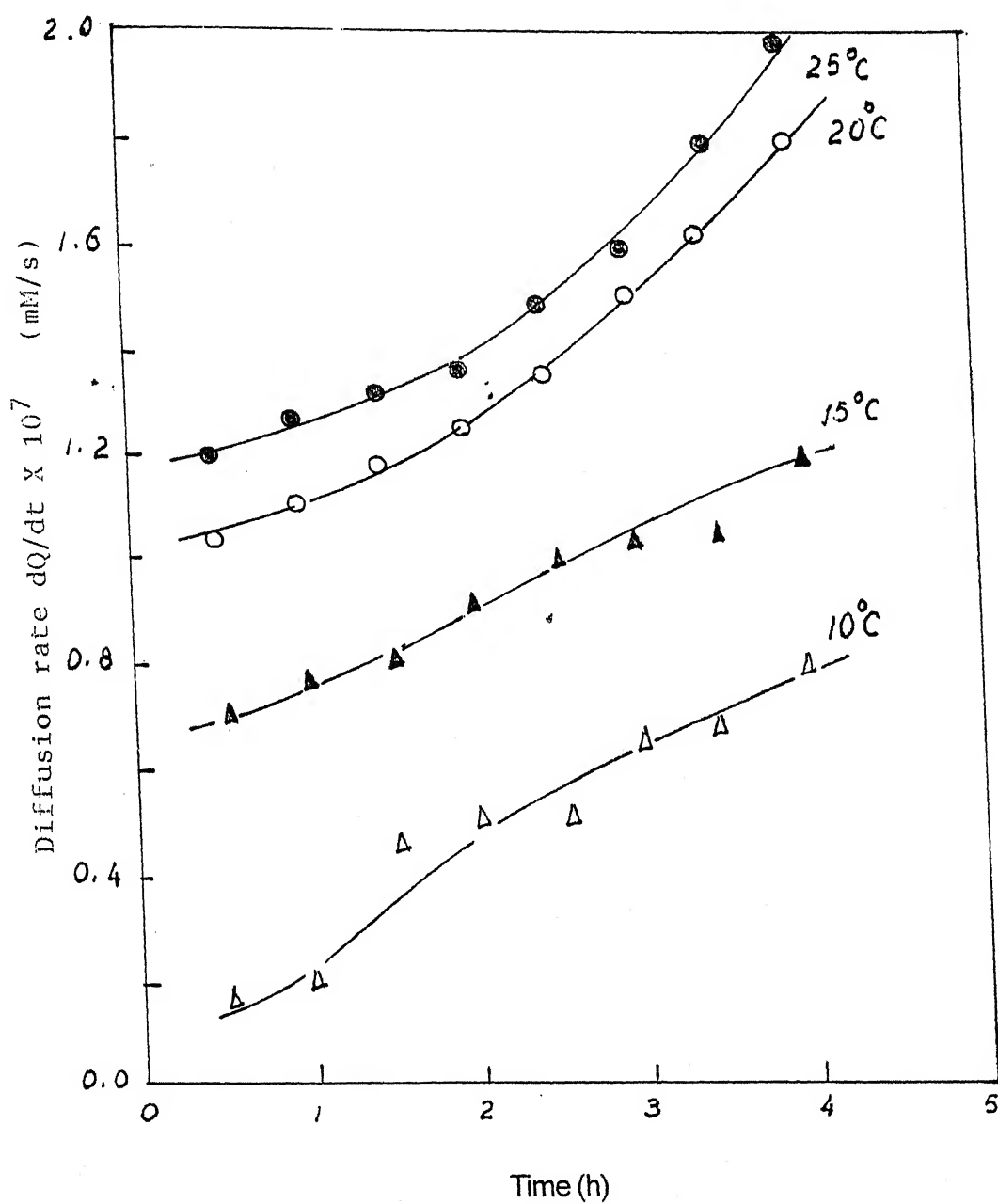


FIG. - 16

Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperature across cobalt sulphide membrane using $BaCl_2$ electrolyte

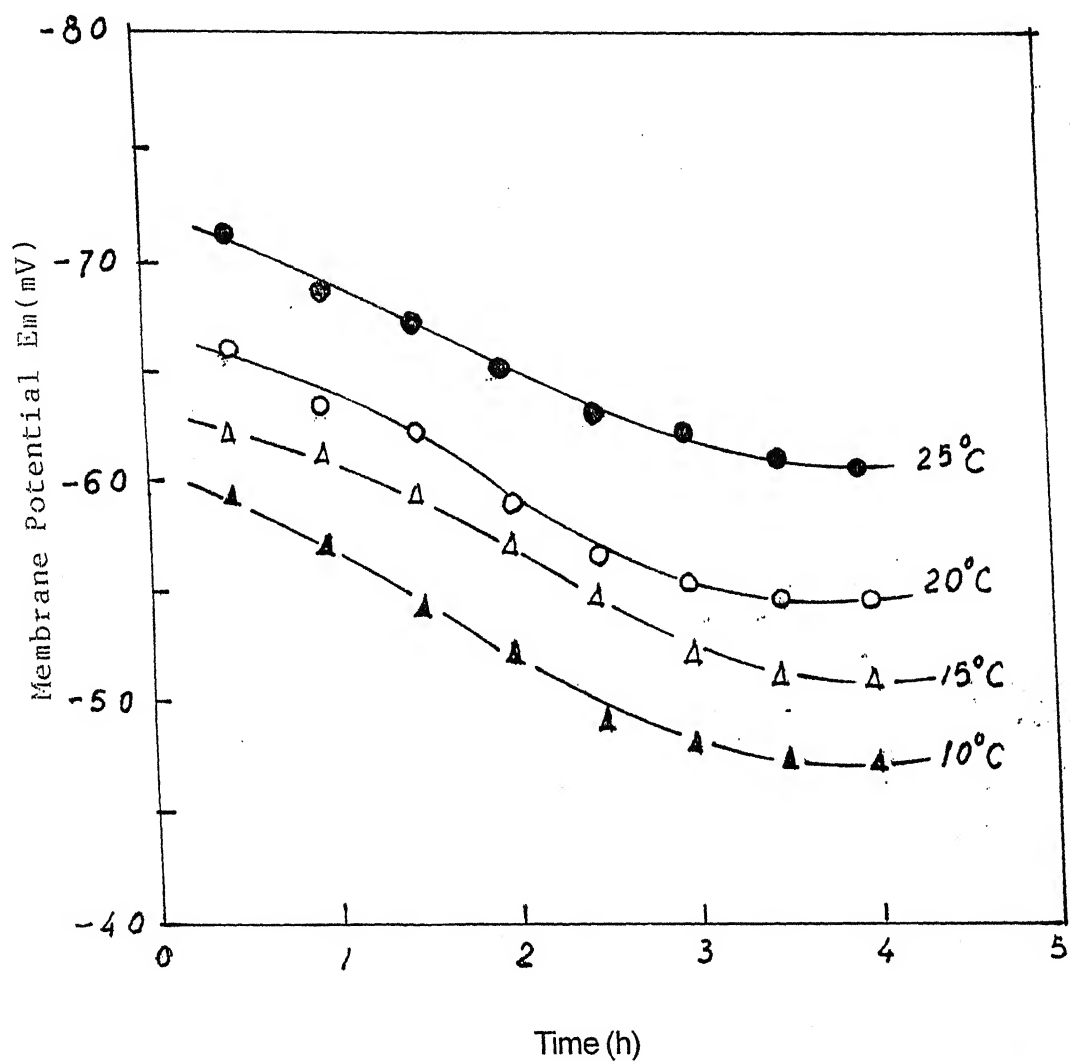


FIG. - 17

Plots of membrane potential E_m (mV) against Time (h) at different temperature across cobalt sulphide membrane using $MgCl_2$ electrolyte.

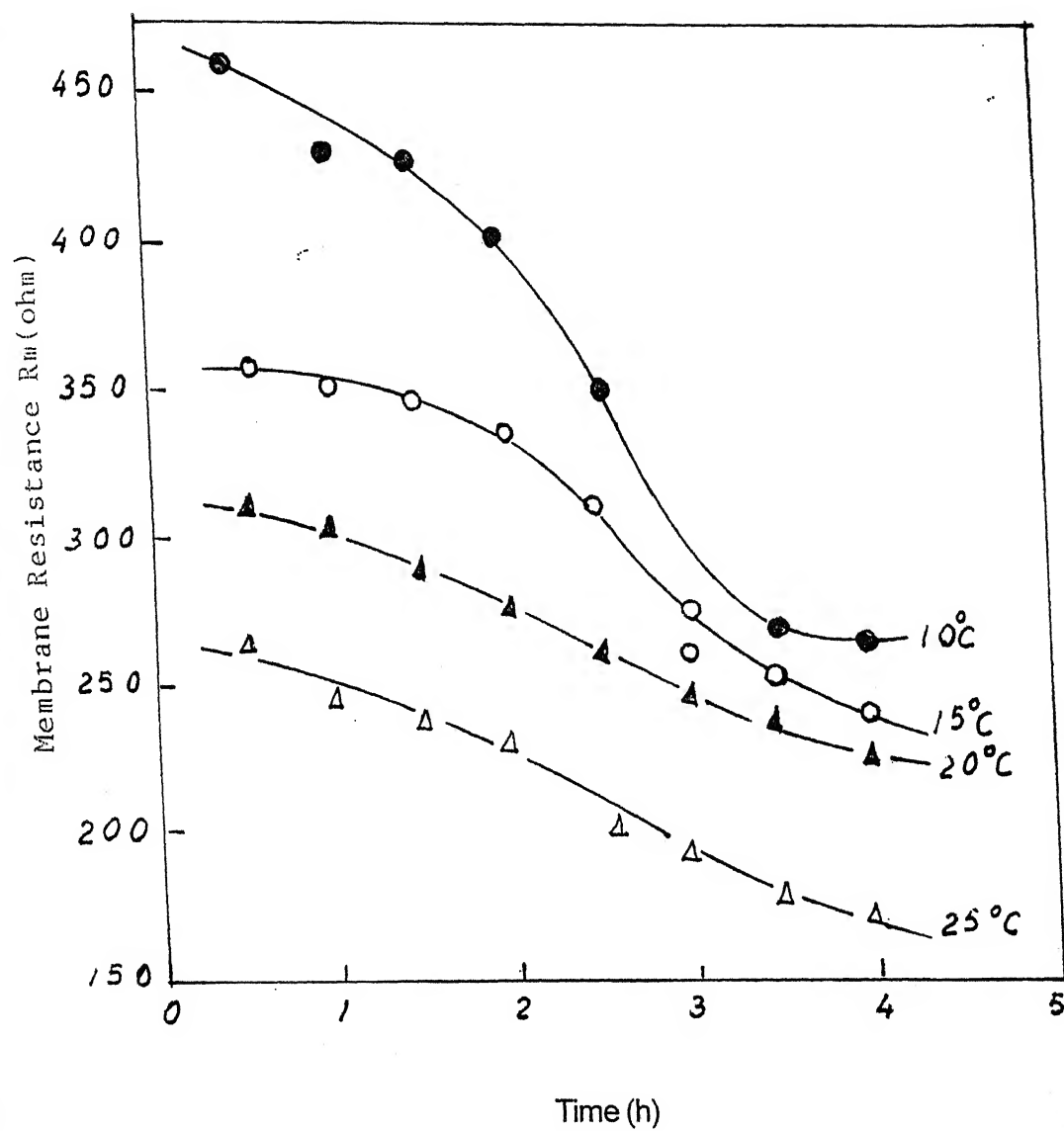


FIG. - 18

Plots of membrane resistance R_m (ohm) against Time (h) at different temperatures across cobalt sulphide membrane using $MgCl_2$ electrolyte.

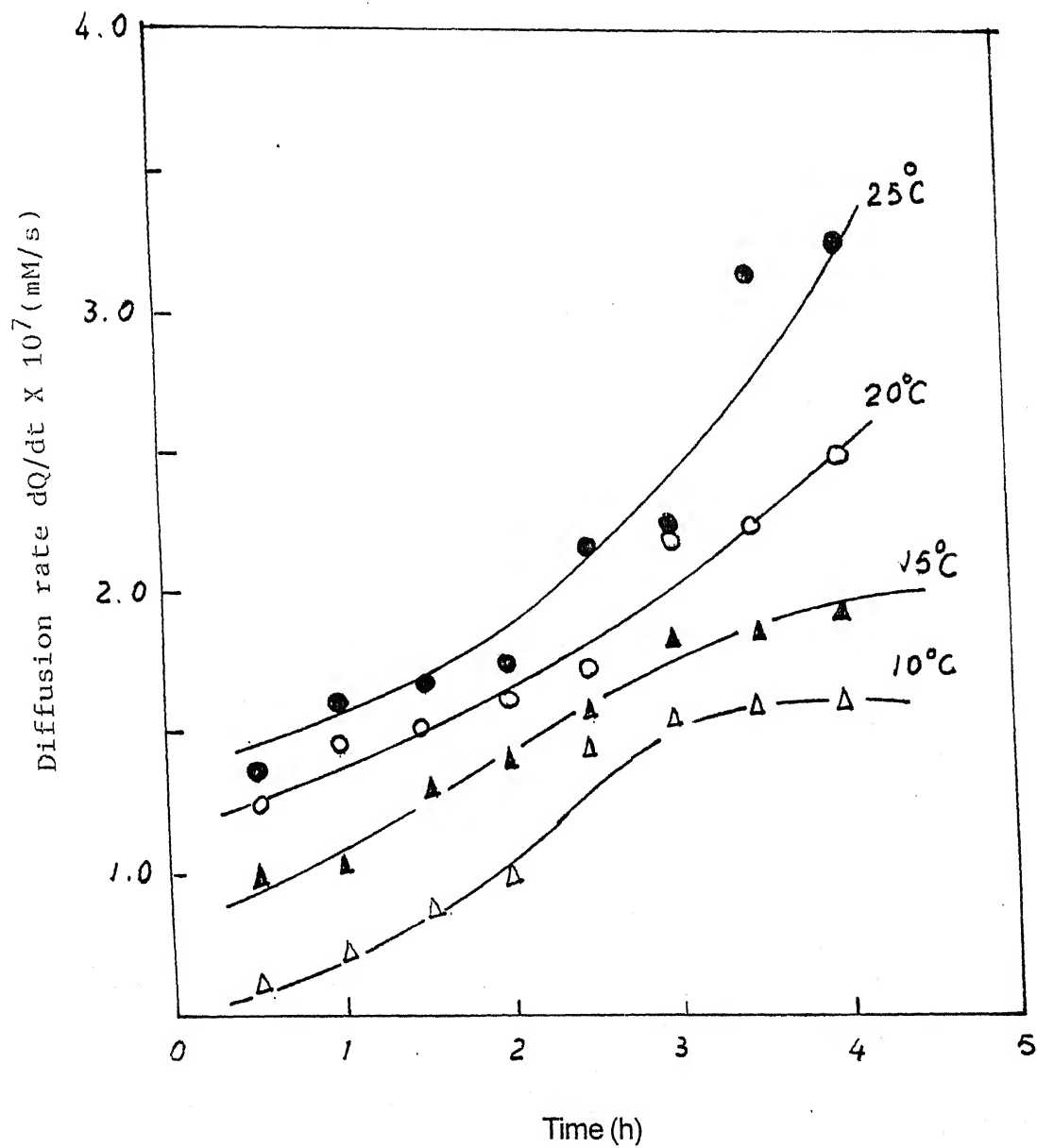


FIG. - 19

Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperature across cobalt sulphide membrane using $MgCl_2$ electrolyte.

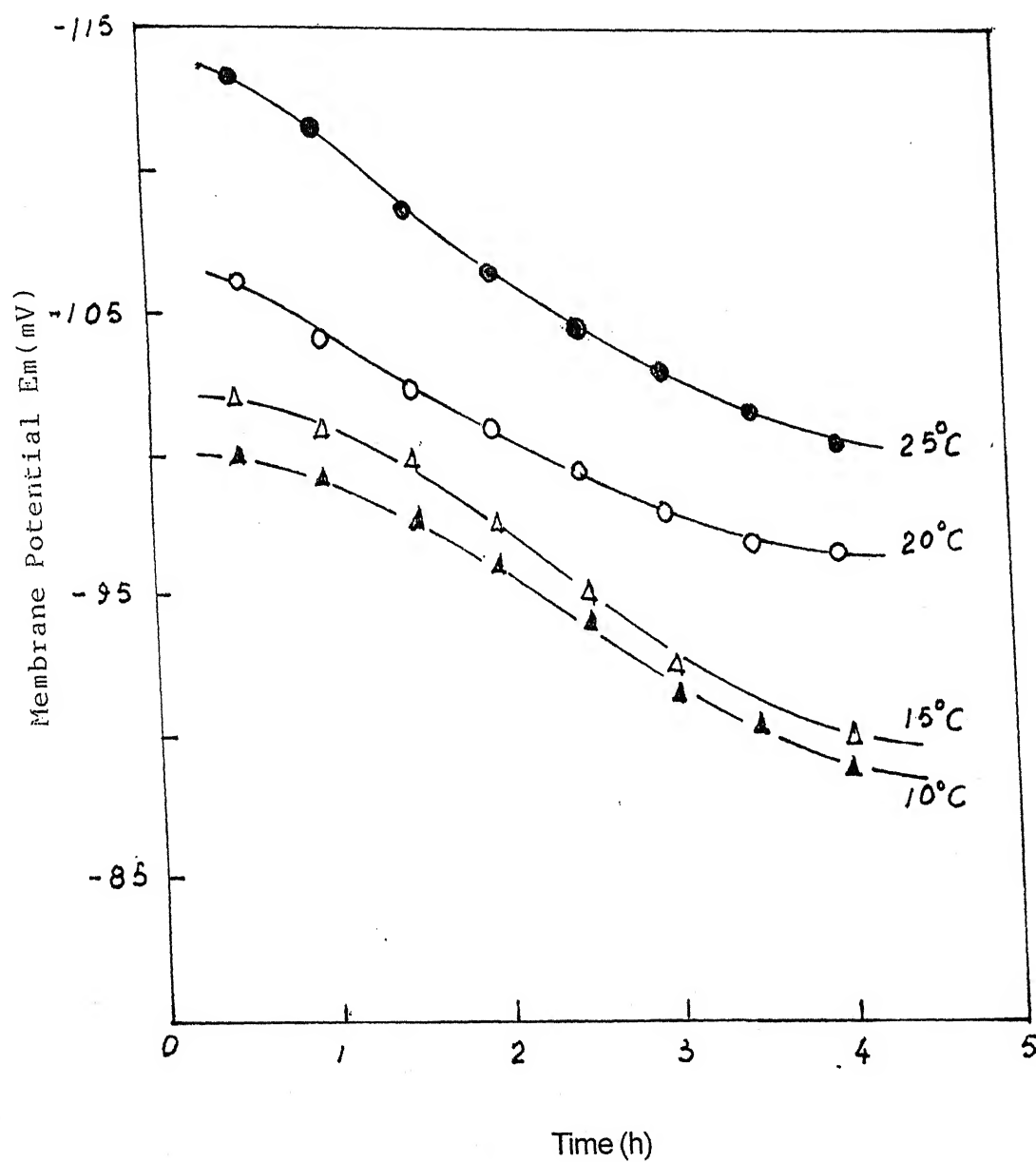


FIG. - 20

Plots of membrane potential E_m (mV) against Time (h) at different temperature across cobalt sulphide membrane using $AlCl_3$ electrolyte.

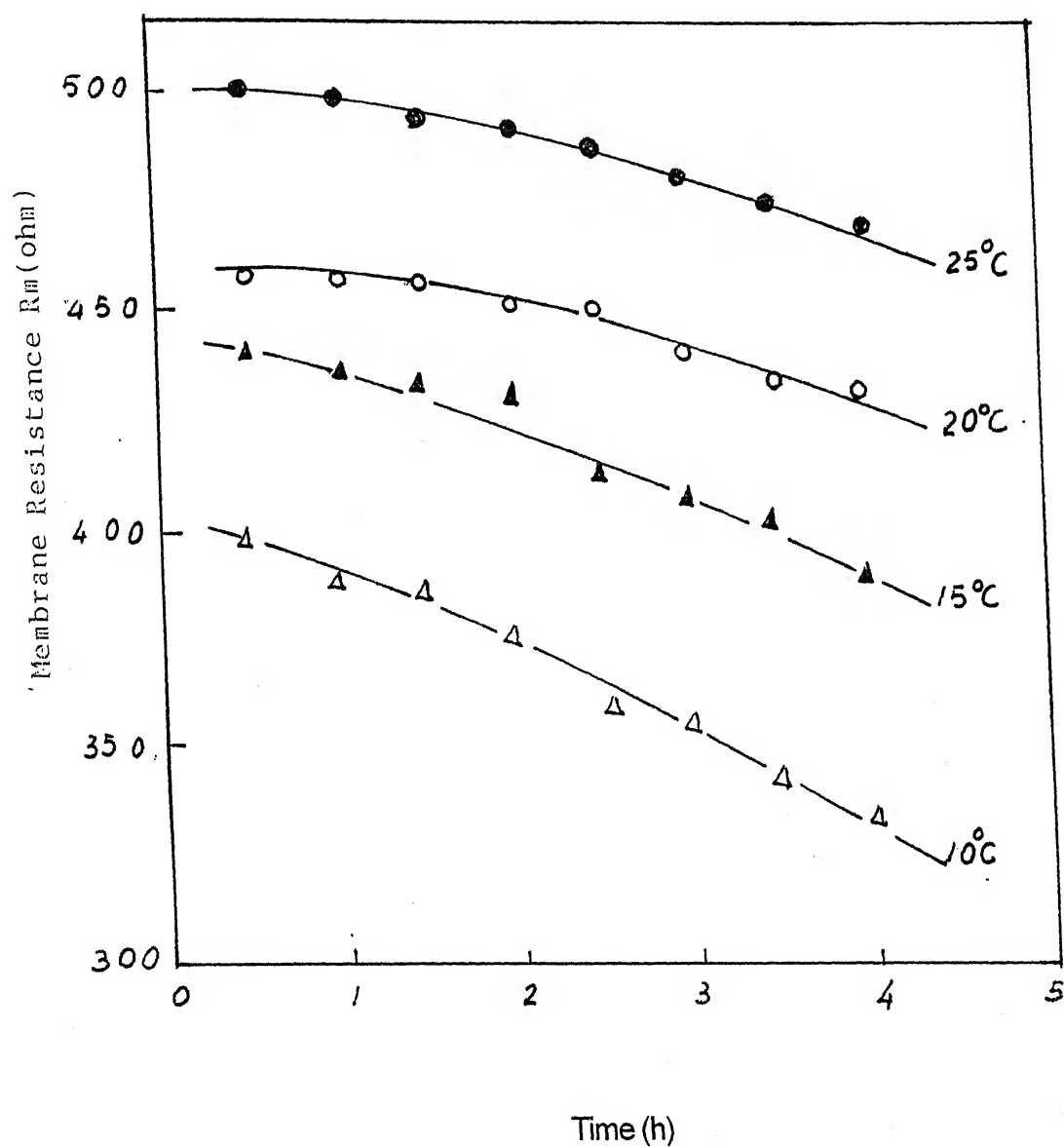


FIG. - 21

Plots of membrane resistance R_m (ohm) against Time (h) at different temperature across cobalt sulphide membrane using $AlCl_3$ electrolyte.

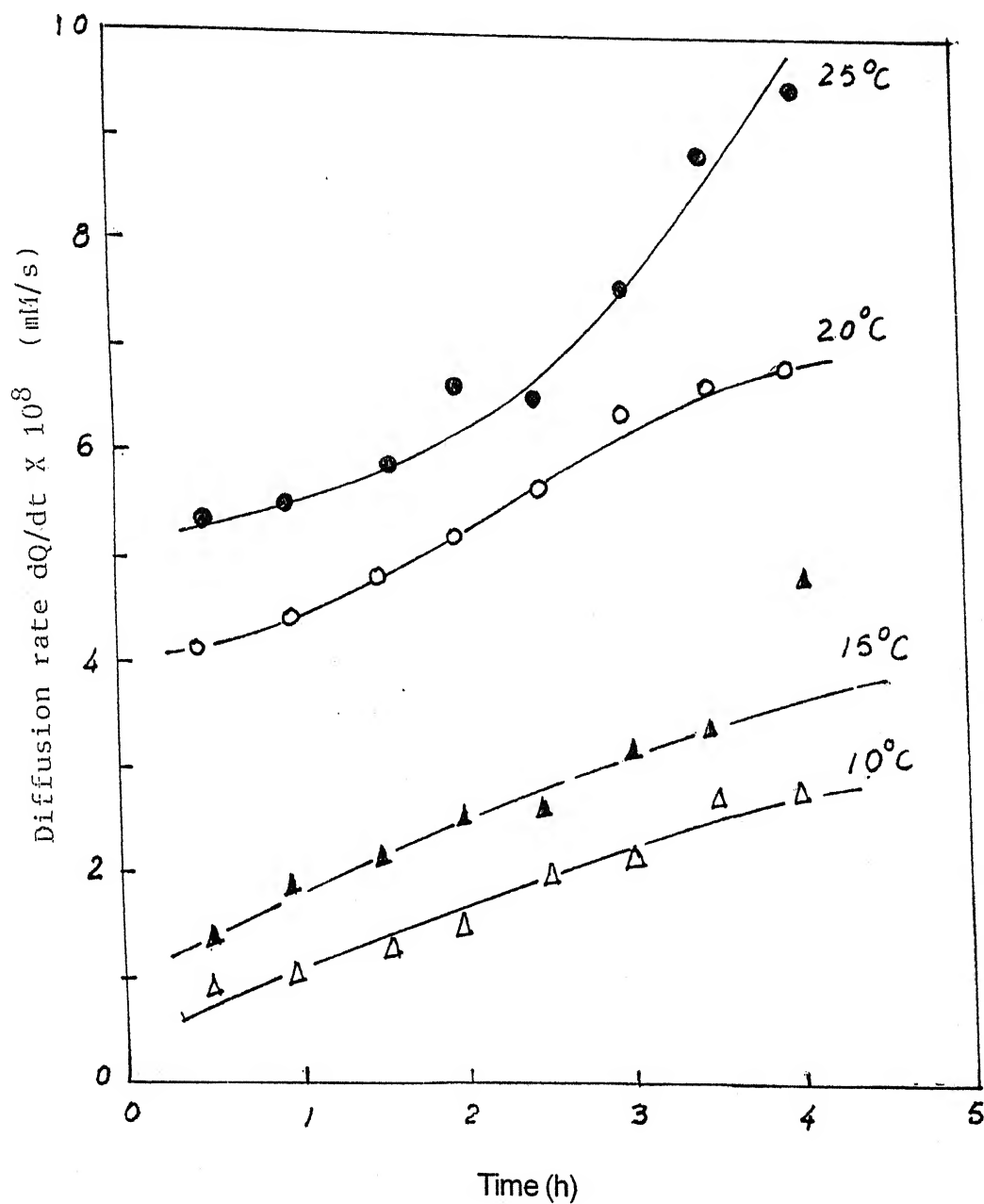


FIG. - 22

Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperature across cobalt sulphide membrane using $AlCl_3$ electrolyte.

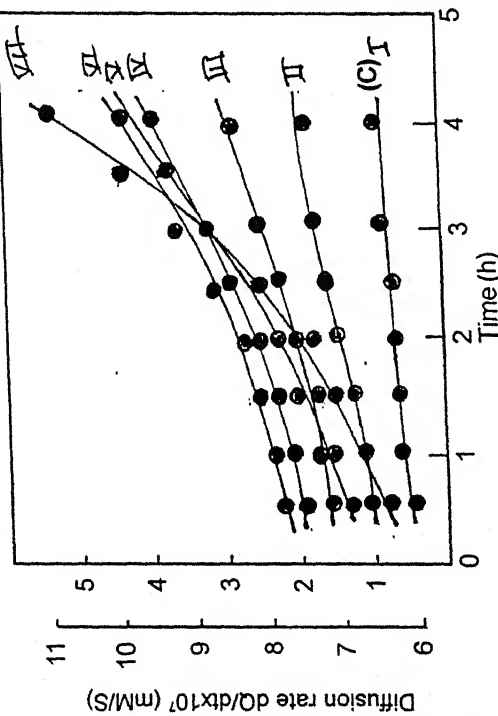
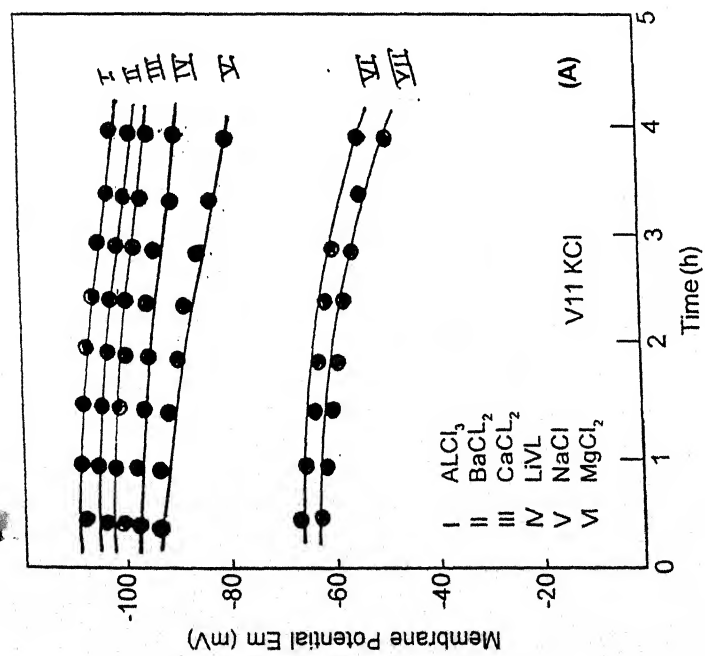


Fig. 23

Fig. 25

Plots of (A) Membrane potential E_m (mV) (B) Membrane Resistance R_m (Ohm) (C) Diffusion Rate $dQ/dtx \cdot 10^7$ (mM/S) against time (h) Across Nickel Sulphide Membrane at $25^\circ C$

Membrane Resistance R_m (ohm)

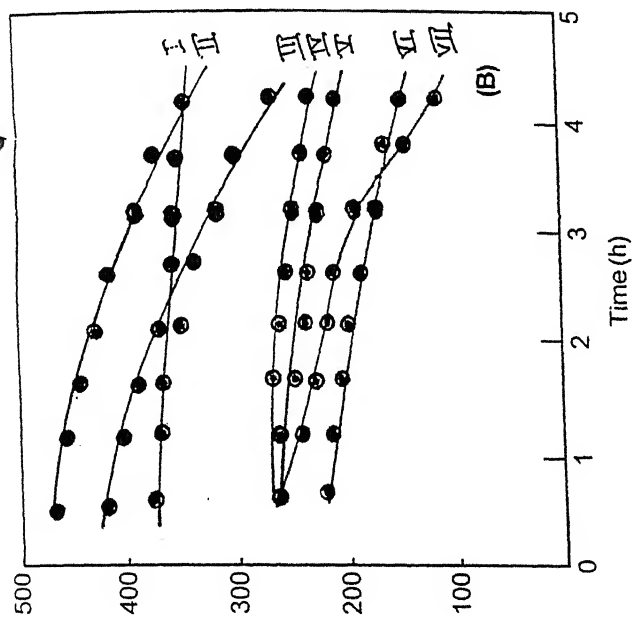


Fig. 24

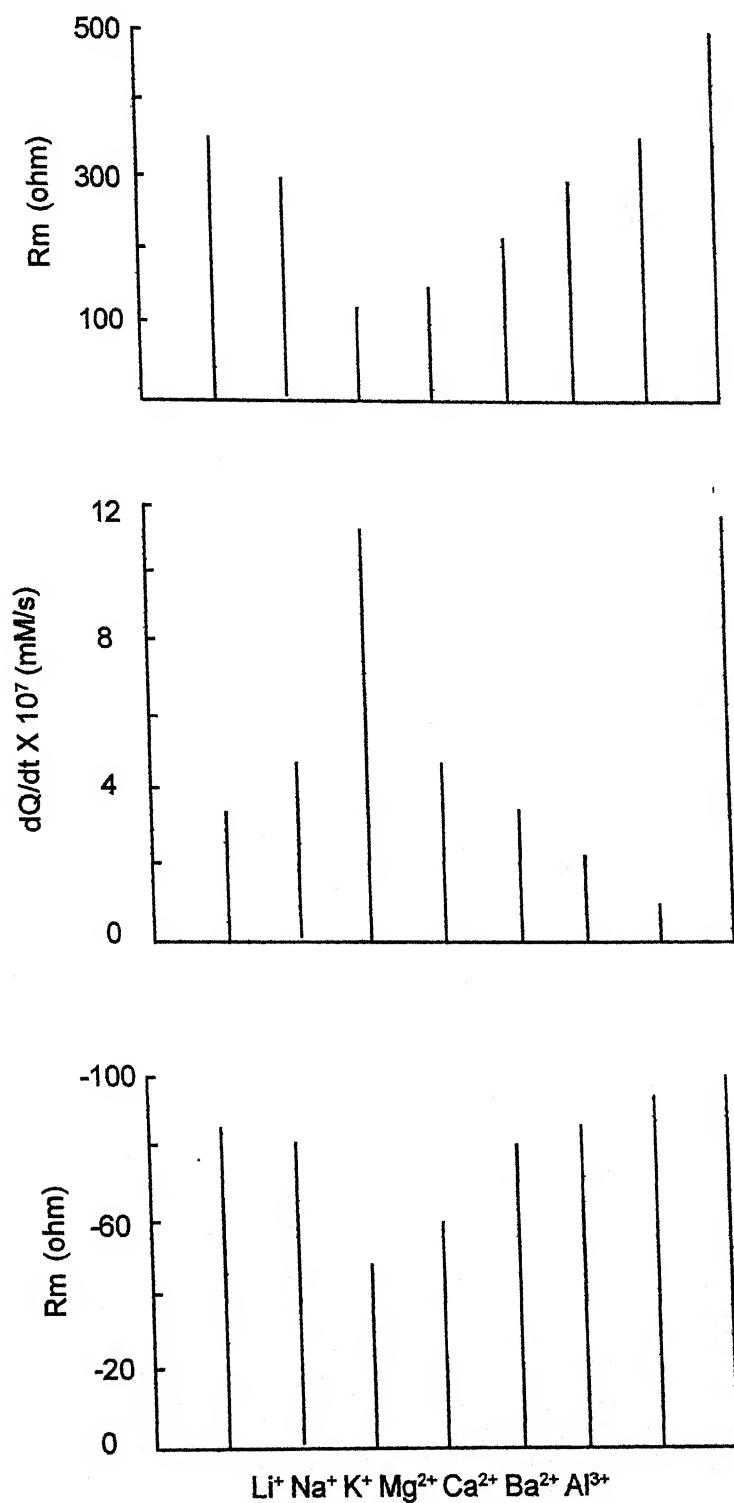


Fig. 26 Plots of E_m , R_m , and dQ/dt against various electrolytes, across nickel sulphide membrane at 25°C .

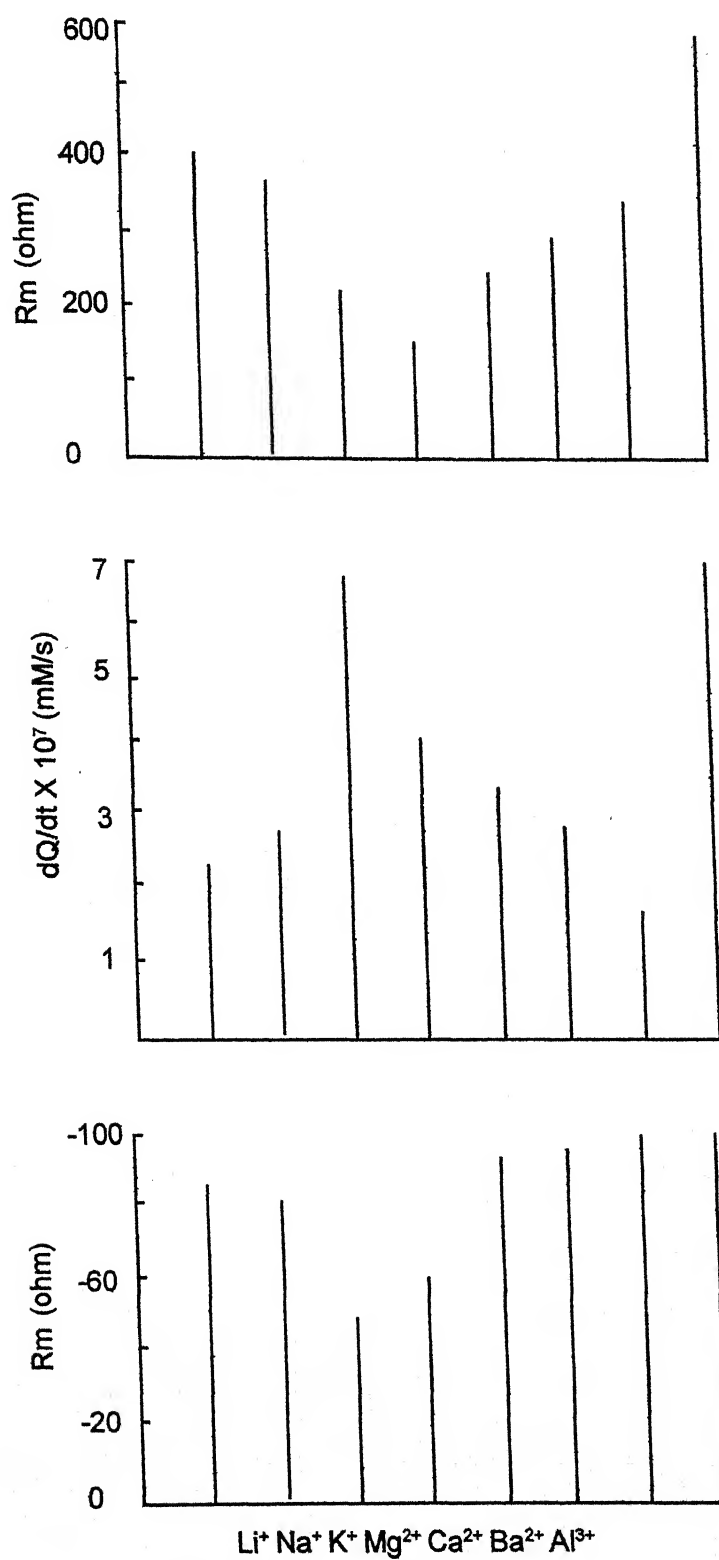


Fig. 27 Plots of E_m , R_m , and dQ/dt against various electrolytes, across cobalt sulphide membrane at 25°C .

increase in the ion association with the membrane exchange groups. This is in agreement with the findings of Subrahmanyam and Lakshminarayanaiah [49] and Gregor and co-workers [50] for the AMF C- 103 membrane and our own findings with parchment supported inorganic precipitate membranes [30,33,35].

The values of E_m decreases with time though almost to a negligible extent, as can be seen, in Fig. 23 for various diffusing electrolytes through parchment supported nickel sulphide membrane. The slight change in E_m may be due to the small changes produced in the concentration of electrolyte solutions during the diffusion process. The membrane potential sequence for alkali metal ions was $Li^+ > Na^+ > K^+$ and for multivalent cations it was $Al^{3+} > Ba^{2+} > Ca^{2+} > Mg^{2+}$. This sequence of membrane potential points towards the fact that multivalent ions are more strongly adsorbed on the membrane skeleton than univalent ions and that aluminium being most strongly adsorbed [30].

The values of diffusion rate dQ/dt for various cations were calculated from the predetermined values of membrane potential E_m and membrane resistance R_m using eqs. [4-6]. The diffusion of electrolytes through the membrane is slower than in free solution. This may be due to various reasons: [a] only a part of framework is available for free diffusion, [b] the diffusion paths in the membrane phase are more tortuous and therefore longer, [c] the larger hydrated ions in the narrow mesh region of the membrane be 'impeded in their mobility by the framework and [d] the interaction of the diffusing species with the fixed groups on the membrane matrix. The diffusion rate sequence of cations diffusing through the

membrane was $K^+ > Na^+ > Li^+ >$ and $Mg^{2+} > Ca^{2+} > Ba^{2+} > Al^{3+}$. This diffusion rate sequence on the basis of Eisenman-Sherry model of membrane selectivity [41,43,51] point towards weak field strength of charge groups attached to the membrane matrix. This is in agreement with our earlier findings of inorganic precipitate membranes [23-31].

Parchment paper, except for the presence of some stray and end carboxyl groups, contains very few fixed groups. Deposition of inorganic precipitate gives rise to a net negative charge on the membrane surface in the case of dilute solutions of electrolyte [1: 1] leading to the type of ionic distribution associated with the electrical double layer. However, use of concentrated electrolyte [1: 1] or [2: 1] or [3: 1] leaves a net positive charge on the membrane surface due to preferential adsorption of cations. This type of charge reversal is not peculiar to these systems. Rosenberg et al. [52] found in the case of thorium counterions, negative electroosmotic transport of water. The ion was so thoroughly adsorbed on a cation exchange membrane that it conferred anion selectivity to the membrane and thus water was transferred in the opposite direction. Similarly Schulz, [53] found, in the case of sodium disulphide, adsorption of the disulphide anion on the surface of the anion exchange membranes permplex A-100. This reversed the charge on the membrane and also the direction of water flow.

The system under consideration may be taken as having charged capillary structures or gels which can be judged in the light of classical fixed charge theory of Teorlls [54]; Meyer and Sievers [55]; Sollner [56]; He et al. [57] Paloty and Hoch et al. [58,59]. Flow of electrolyte by diffusion because of the presence of a net charge [-ve or + ve] on the membrane gives

rise to the membrane potential as opposed to the liquid junction potential ordinarily under similar conditions in the absence of the membrane, which regulates the flow of electrolyte by increasing the speed of slow moving ion and by decreasing the speed of the faster moving ion. The regulated rate of flow for various electrolytes through the investigated membranes follow the sequence $K^+ > Na^+ > Li^+$ and $Mg^{2+} > Ca^{2+} > Ba^{2+} > Al^{3+}$.

Membrane porosity in the relation to the size of the species [hydrated] flowing through the membrane seems to determine the above sequence. Although the sizes of the hydrated electrolytes are not known with certainty, because of few tabulations [60-61] of the number of moles of water associated with some electrolytes. However, in Fig. 28 a plot of permeability of different electrolytes [chlorides] against free energy of hydration of cations [62] is given for both the membranes. It is seen that permeability decreases with increasing hydration energy, that is, greater size due to "increase in hydration. This points to the fact that the electrolyte is diffusing along the 'pores or channels of dimensions adequate enough to allow the substance to penetrate the membrane. The state of hydration of penetrating electrolyte may be considered to exist in a dynamic condition so that at higher temperatures considerably higher fraction 'F' of the total number of a given kind would possess excess energy, ΔE according to the Boltzman distribution $f = e^{-\Delta E/RT}$ [R is the gas content]. Under these circumstances, those ionic species which have lost sufficient water of hydration to be smaller than the size of the pore would enter the membrane. In this way, the permeability would increase with increase in temperature, subject, however, to the proviso so that the membrane has undergone no irreversible change in its

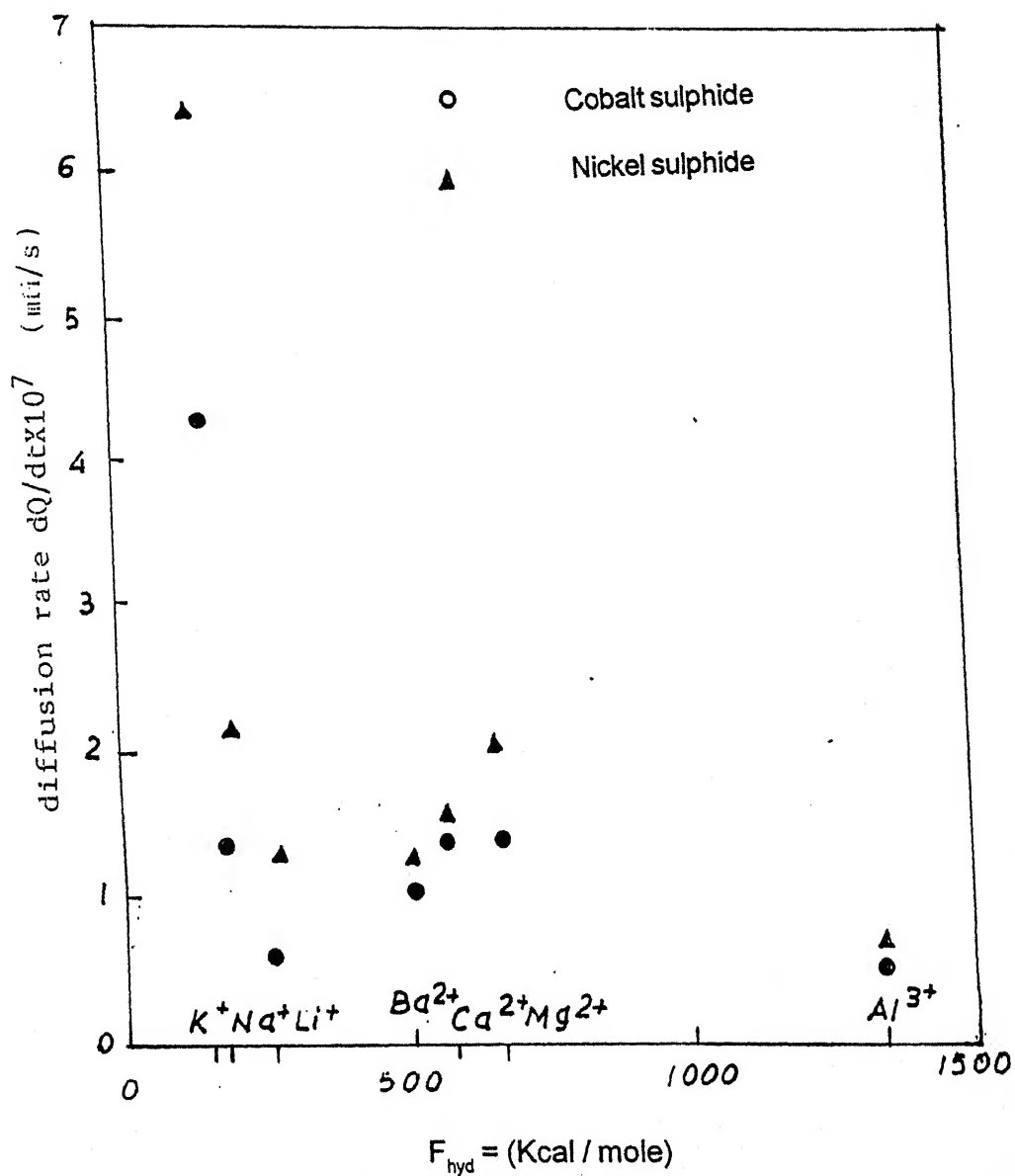


FIG. - 28

Diffusion rate $dQ/dt \times 10^7$ (mM/s) at 25°C for various electrolytes (Chloride) through both the membrane plotted against free energy (F^*) of hydration of cations.

structure. That no such structural change is involved is evident from the linear plots of $\log dQ/dt$ versus $[1/T]$ given in Figs 29 and 30. The slope of these lines which is equal to $[E_a/2.303 R]$ gave the activation energy E_a required for the diffusion process. The values so derived are given in tables 31 and 32. The diffusion rate dQ/dt [millimol/h] is related to diffusion coefficient D [cm/sec] by the relation

$$\bar{D} = \frac{dQ}{dt} \times \frac{10^{-6}}{3.6} A \Delta C \quad [7]$$

where A is the membrane area [24.6 Cm^2] and ΔC is the difference in the electrolyte concentration existing across the membrane. Since area of membrane and concentration difference of the electrolytes are constants therefore D is proportional to dQ/dt and thus the slopes of linear plots of $\log \bar{D}$ vs $[1/T]$ and of $\log dQ/dt$ Vs. $[1/T]$ will be equal.

The theory of absolute reaction rate [45] has been applied to diffusion processes in membrane by several investigators [44-46, 62-64]. According to Zolinsky et al. [44], we have

$$\bar{D} = \lambda^2 (KT/dh) \exp - F^\ddagger / RT \quad [8]$$

where K is Boltzman constant, d is. membrane thickness, h is plank constant, and λ is average distance between equilibrium positions in the process of diffusion.

ΔF^\ddagger is the free energy of activation for diffusion and is related to enthalpy ΔH^\ddagger and ΔS^\ddagger of activation of diffusion by Gibbs Helmholtz equation

$$\Delta F^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad [9]$$

ΔH^\ddagger is related to Arrhenius energy of activation E_a by the equation

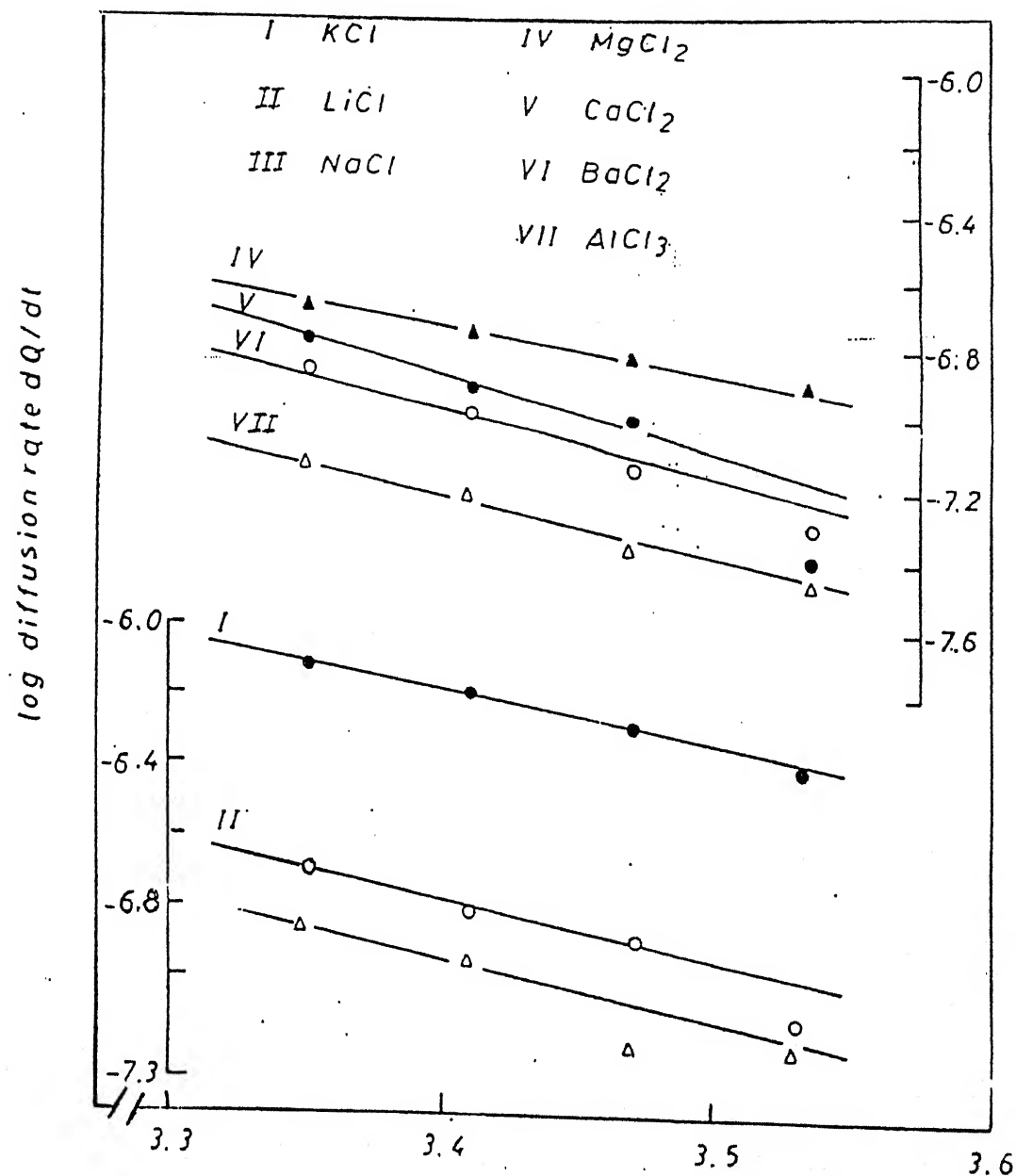


FIG. 29

Plots of dQ/dt against $1/T$ for various electrolytes across cobalt sulphide membrane at $25^\circ C$

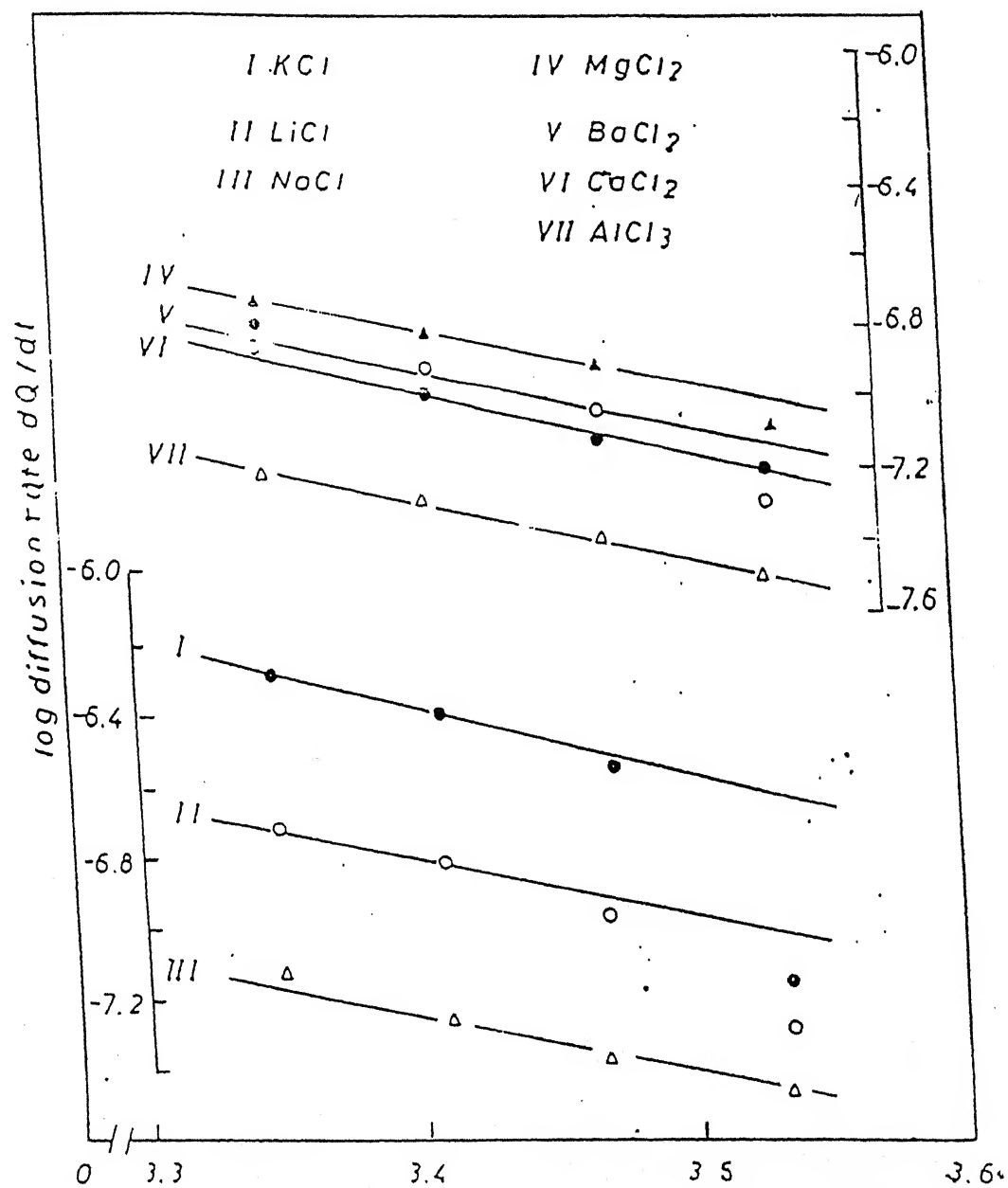


FIG. 30

Plots of dQ/dt against $1/T$ for various electrolytes across Nickel Sulphide membrane at 25°C

Table 31
Experimental activation energy E_a and other Thermodynamic parameters
calculated from transition state Theory of rate processes For Cobalt
Sulphide Membrane at $25 \pm 0.1^\circ\text{C}$

Parameter Electrolyte	E_a (Kcal Mol ⁻¹)	ΔH^\ddagger (Kcal Mol ⁻¹)	ΔF^\ddagger (Kcal Mol ⁻¹)	ΔS^\ddagger (e.u.)
KCL	6.40	5.80	10.00	-13.00
NaCl	5.70	5.10	10.30	-16.50
LiCl	5.40	4.80	10.80	-19.20
CaCl ₂	4.90	4.40	10.70	-20.40
BaCl ₂	5.10	4.50	10.90	-20.50
MgCl ₂	4.10	3.50	10.70	-23.50
AlCl ₃	3.90	3.30	11.40	-26.20

Table 32
Experimental activation energy E_a and other Thermodynamic parameters
calculated from transition state Theory of rate processes For Nickel
Sulphide Membrane at $25 \pm 0.1^\circ\text{C}$

Parameter Electrolyte	E_a (Kcal Mol ⁻¹)	ΔH^\ddagger (Kcal Mol ⁻¹)	ΔF^\ddagger (Kcal Mol ⁻¹)	ΔS^\ddagger (e.u.)
KCL	6.10	5.50	9.80	-13.30
NaCl	5.70	5.10	10.80	-18.20
LiCl	5.20	4.60	10.60	-19.00
CaCl ₂	4.90	4.30	10.70	-20.60
BaCl ₂	4.60	4.00	10.90	-22.40
MgCl ₂	4.50	3.90	10.60	-21.40
AlCl ₃	3.60	3.00	11.30	-26.80

Vide Figs. 31 - 33

$$\Delta H^\ddagger = E_a - RT$$

[10]

As the values of d and of the universal constants are known, values of, ΔH^\ddagger , ΔS^\ddagger , and ΔF^\ddagger can be calculated provided the value of λ is, known. Different investigators [44-46,63,65] have used values ranging from 1.5 A° for λ . In this work a value of 1 A° has been used in calculations, and the values so derived for the different thermodynamic parameters are given in Tables 31 and 32. For purpose of comparison, in Table 33 are given the values of ΔS^\ddagger determined by various investigators for a variety of systems. The values of ΔS^\ddagger [see Table 33] are either positive or negative for membranes. There are few values which are close to zero and correspond to liquid systems. According to Eyring and co-workers [44,45], the values of ΔS^\ddagger indicate the mechanism of flow; large positive ΔS^\ddagger is interpreted to reflect breakage of bonds, while low values indicate either formation of covalent bond between the permeating species and membrane material or that the permeation through the membrane may not be rate determining step.

On the contrary, Barrer [63,66,67] has developed the concept "zone activation" and applied it to the permeation of gases through polymer membranes. According to this zone hypothesis, a high ΔS^\ddagger , which has been correlated with high energy of activation for diffusion, means either the existence of a large zone of activation or the reversible loosening of more chain segments of the membrane. A low ΔS^\ddagger , then means either a small zone of activation or no loosening of the membrane structure on permeation. In view of these differences in the interpretation of ΔS^\ddagger , Shuller et al. [46], who found negative ΔS^\ddagger value for sugar permeation through collodion

Table 33
Thermodynamic Parameters ΔS^\ddagger For permeation of various substances
Through different systems.

Diffusing Species	Diffusion system Medium	Entropy factor $\lambda [e\Delta S^\ddagger / R], r^2$ A_0	ΔS^\ddagger , e.u.	Reference
Water	Water	10.0	8.5	
Phenol	Methyl alcohol	0.4	0.3	
Phenol	Benzene	0.4	0.3	31b
C ₂ H ₂ Br ₄	C ₂ H ₂ Cl ₄	0.00	0.00	
Bromine	CS ₂	0.4	-2.6	
Mannitole	Water	1.8	3.1	50b ^b
H ₂	Butadiene-acrylonitrile Membrane	181	15.0	
N ₂	Butadiene-acrylonitrile Membrane	129	13.7	
N ₂	Butadiene-methyl meth-acrylate Membrane	149	14.3	31 ^b 52 ^c
Ar	Butadiene-methyl meth-acrylate Membrane	92	12.4	
N ₂	Butadiene-polystyrene Membrane	23	6.8	
Ar	Butadien-polystyrene Membrane	32	8.3	
H ₂	Neoprene Membrane	73	11.4	
N ₂	Neoprene Membrane	214	15.7	31 ^b 52 ^c
Ar	Neoprene Membrane	184	15.2	
H ₂	Chloroprene Membrane	149	14.3	
H ₂	Silicone rubber Membrane (Sheet)	0.3	-2.4	
N ₂	Silicone rubber Membrane (Sheet)	0.84	-4.0	
O ₂	Silicone rubber Membrane (Sheet)	0.60	-5.3	53
He	Silicone rubber Membrane (Sheet)	0.86	-4.9	
Ar	Silicone rubber Membrane (Sheet)	0.82	-4.1	
H ₂	Glass Membrane	4x10 ⁻²	-16.1	
He	Glass Membrane	4x10 ⁻²	-16.1	32
Sucrose	Collodion Membrane	1.1x10 ⁻²	-22.2	
Lactose	Collodion Membrane	4.3x10 ⁻²	-16.8	
Mannitol	Collodion Membrane	8.1x10 ⁻³	-23.4	32
Raffinose	Collodion Membrane	2.4x10 ⁻²	-19.1	
H ₂ O (Source Solution)	Collodion Membrane	1.2x10 ⁻²	-21.8	
H ₂ O	n-Hexadecane liquid	2.8	-0.2	55

H ₂ O	Hexamethyltetracoson liquid	4.8	1.9	
H ₂ O	Polyethylene Membrane	3.9×10^3	28.4	56
H ₂ O	Polyethylene Membrane	25×10^3	35.8	
H ₂ O	Liquid bilayer Membrane (Oxidized cholesterol)	5.5×10^{-2}	-15.8	51
H ₂ O (Endo-osmosis)	Arbacia eggs (unfertilised)	14.4×10^3	3.16	
Propionamide	Arbacia eggs (unfertilised)	26.9×10^3	34	30 ^d
Butyramide	Arbacia eggs (unfertilised)	12.1×10^4	40	
Nonelectrolyte (glycerol, glycols, thiourea)	Oxerythrocyte Membrane	77	3.7	50 ^b

a All results correspond to $\lambda = 3 \text{ \AA}^0$ unless otherwise noted

b Calculations correspond to $\lambda = 31 \text{ \AA}^0$

c Calculations correspond to $\lambda^2 = 10^{-15} \text{ cm}^2$

d Calculations correspond to $\lambda = 5 \text{ \AA}^0$

membrane, have stated that "it would probably be correct to interpret the small negative value of ΔS^\ddagger mechanically as interstitial permeation of the membrane [minium chain loosening] with partial immobilization in the membrane[small zone of disorder]". On the other hand, Tien and Ting [65] who found negative ΔS^\ddagger values for the permeation of water through very thin [50 Å thickness] bilayer membrane, stressed the possibility that the membrane may not be the rate-determining step. Based on additional experimental data, they come to the conclusion that the solution-membrane interface was the rate-limiting step for permeation.

The result of our investigations, Table 31 and 32 indicate that electrolyte permeation gives rise to negative values for ΔS^\ddagger for both the membranes show the similar behaviour for different electrolytes. It is in general found that as the valence of the individual ion is increased, the decrease in the value of ΔS^\ddagger is enhanced.

Since the membranes used in this study are fairly thick compared to bilayers. It is believed that the membrane alongwith solution-membrane interface controlled the electrolytes permeation with partial immobilization in the membrane, the partial immobility increasing in a relative manner with increase in the valence of the ion constituting the electrolyte.

In Figs. 31-33, the individual ionic distribution to the property of aqueous ions given by Noyes [68]: namely $\Delta H_{\text{hydration}}$, $\Delta F_{\text{hydntion}}$, $\Delta S_{\text{hydration}}$ Li^+ , Na^+ , K^+ as well as those of Ba^{2+} , Ca^{2+} and Mg^{2+} are plotted against the corresponding ΔH^\ddagger , ΔS^\ddagger , and ΔF^\ddagger values for diffusion through the membranes. It is found that at least some formal relationship exists between these thermodynamic parameters.

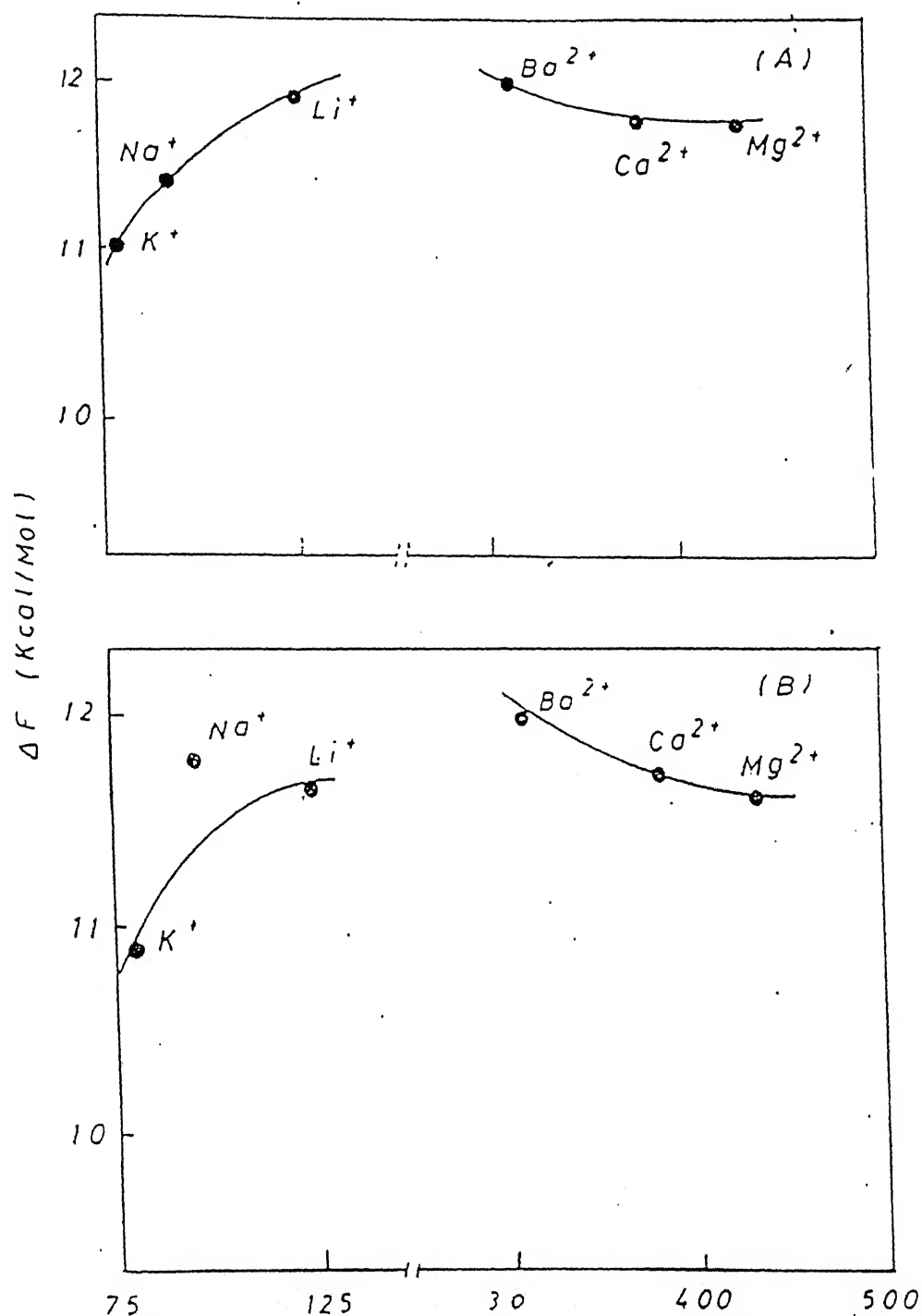


FIG. 31

Plots of ΔF # (Kcal/Mol) for the diffusion of various electrolytes (at 25°C) against ΔF_{hyd} (Kcal/Mol) for respective cations through (A) Cobalt Sulphide and (B) Nickel Sulphide membranes

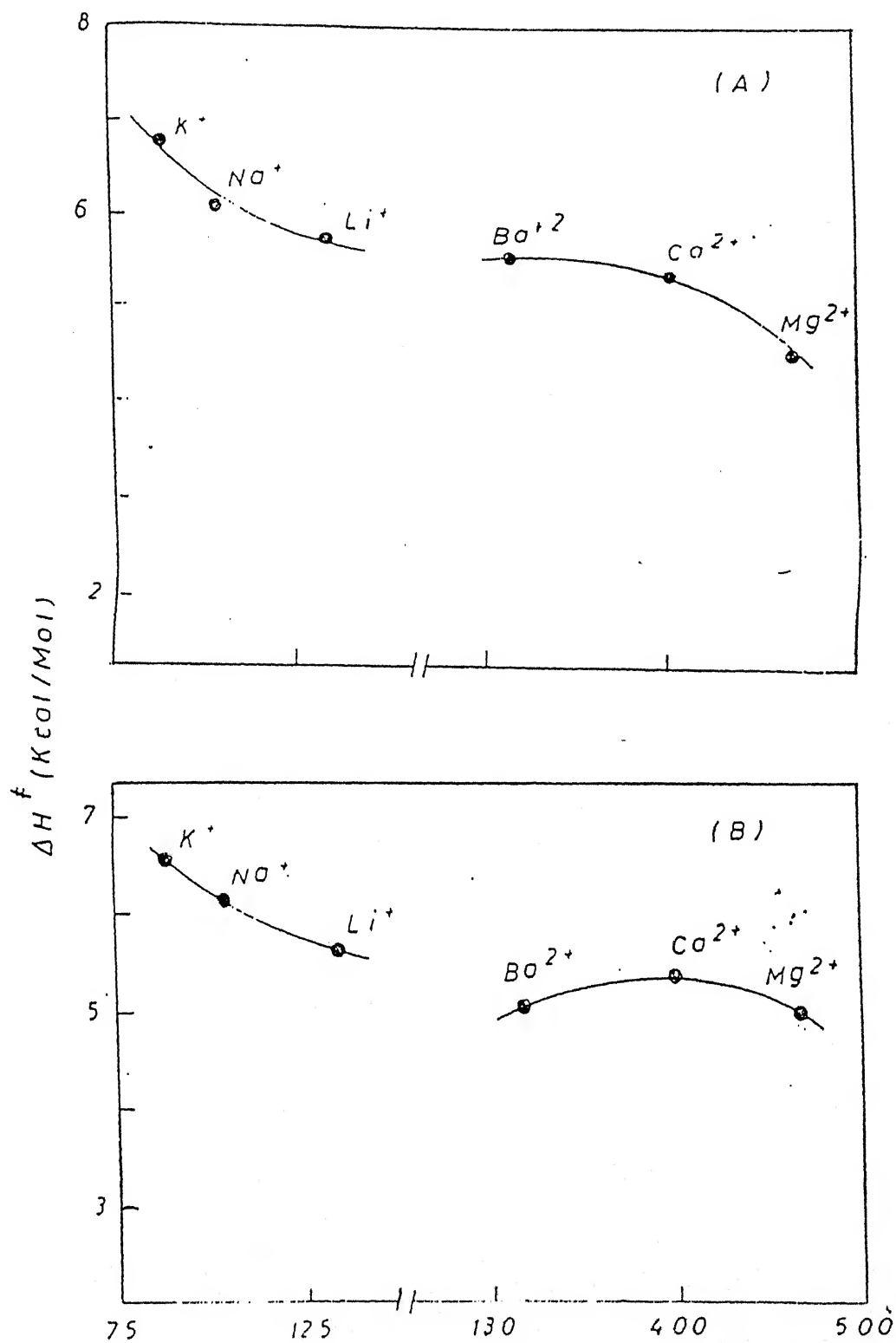


FIG. 32

Plots of ΔH° (Kcal/Mol) for the diffusion of various electrolytes (at 25°C) against ΔH_{hyd} (Kcal/Mol) for respective cations through (A) Cobalt Sulphide and (B) Nickel Sulphide membranes

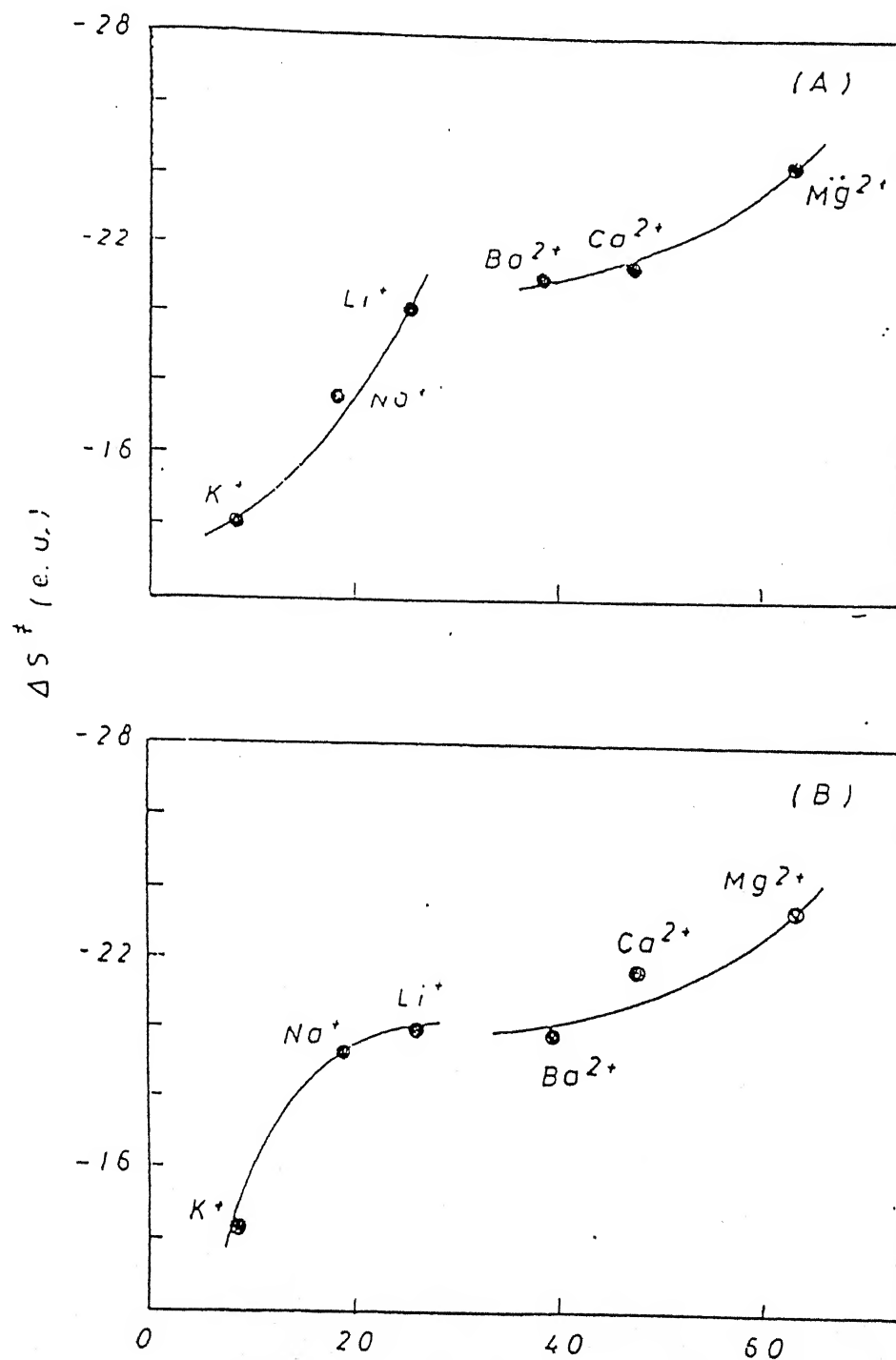


FIG. 33

Plots of ΔS^\ddagger (e.u.) for the diffusion of various electrolytes (at 25°C) against ΔS_{hyd} (Kcal/Mol) for respective cations through (A) Cobalt Sulphide and (B) Nickel Sulphide membranes

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CHAPTER-2

MEMBRANE CHARGE DENSITY

INTRODUCTION

One of the most consistent properties of biological system is the presence of a voltage across the cellular surfaces. The mechanism where by this potential arises is still in dispute. Some consider it to be diffusion potential while others suggest the voltage to be an adsorption potential [1]. Teorell [2,3] considered the presence of charge on the membrane skeleton responsible for the development of potential across it. Based of fixed charge concept a number of theoretical equations for membrane potential, developed across a charged membrane separating two electrolytic solutions, have been derived and tested using, generally, model membranes.

Chakravarti et al. [4] Characterised the membranes by determining the effective fixed charge density of cation exchange membranes by three different methods based on non-equilibrium thermodynamics. Kehar Singh et al. [5] used the mixture of electrolytes for the measurement of membrane potential and evaluated charge density of the membranes for their characterization. Similarly, many investigators [6-8] have also got their peculiar position regarding the electro chemical characterization of different types of membranes with the help of various theories derived for membrane electrical potential and conductance values based on the irreversible thermodynamics.

In this chapter, the evaluation of effective fixed charge density of parchment supported nickel and cobalt sulphide membranes from potential measurements and using the most recently developed methods of

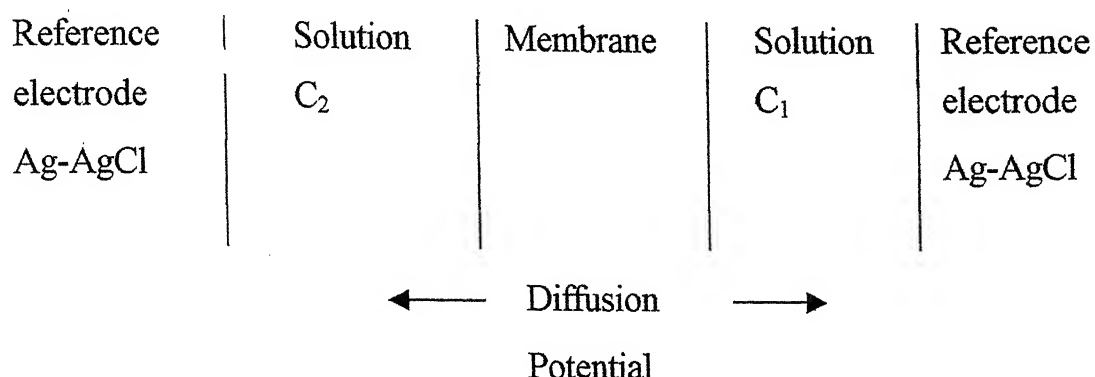
Kobatake et al. [9-20], and Tasaka et al. [21] including the generally used and widely accepted method of Teorell-Meyer and Sievers [2,3] are described. This is in order to substantiate our earlier findings, on the basis of Eisenman-Sherry model of membrane selectivity, that parchment supported membranes possess small density of fixed charge groups on the membrane matrix as well as to test the validity of the recently developed theories for membrane potential.

EXPERIMENTAL

Parchment supported cobalt sulphide and nickel sulphide membranes were prepared by the method of interaction suggested by Kushwaha et. al. [24] and were used here for membrane potential measurements. Solutions used for the preparation of cobalt and nickel sulphide membrane were as follows:

Membrane	Solution I	Solution II
Cobalt sulphide	Co [II] chloride [0.2M]	Sodium sulphide [0.2M]
Nickel sulphide	Ni [II] chloride [0.2M]	Sodium sulphide [0.2M]

The membranes were washed with demonized water to remove free electrolytes completely electro chemical cells of the type



were used for measuring membrane potentials. The reference electrodes used were reversible Ag-AgCl standing in chloride solutions. The total potential difference between Ag-AgCl electrodes placed on either side of the membrane is the algebraic sum of the electrode potential, i.e., concentration potential and the membrane potential E_m [22,23]. A tenfold difference in concentration of chloride solutions [i.e., $C_2/C_1=10$] was maintained and measurements were made by a pye-precision potentiometer [No. 7568]. The solutions were replaced by fresh solutions and when there was no change in potential with the addition of fresh solutions, with constant vigorous stirring by a pairs of magnetic stirrers. It was taken as the true total potential difference across the Ag-AgCl electrodes. In both the membranes it could be reproduced within a few tenths of an mV. The whole cell was immersed in a water thermostat maintained at $25 \pm 0.1^\circ\text{C}$. The various salt solutions [Chlorides of Li^+ , Na^+ and K^+] were prepared from BDH, AR grade chemicals and deionized water.

RESULT AND DISCUSSION

The values of membrane potential E_m measured experimentally across both cobalt sulphide and nickel sulphide membranes are given in Tables 1 and 2, and are also plotted in Figs. 1 and 2 against $\log [C_1+C_2]/2$.

Table 1

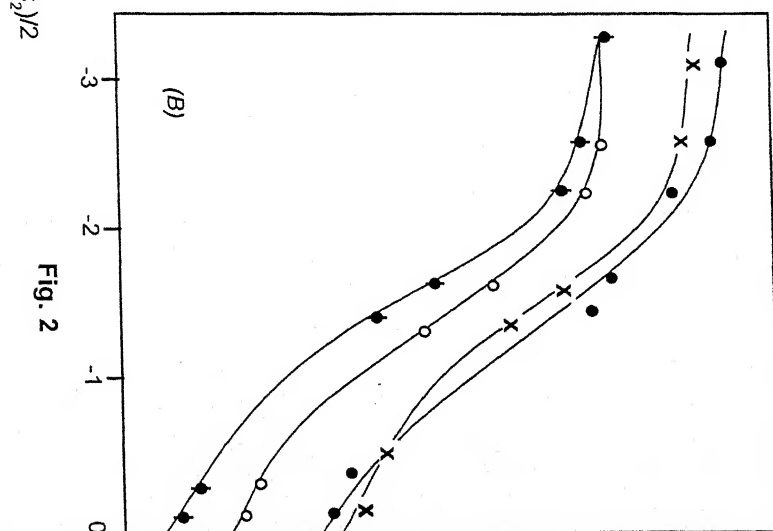
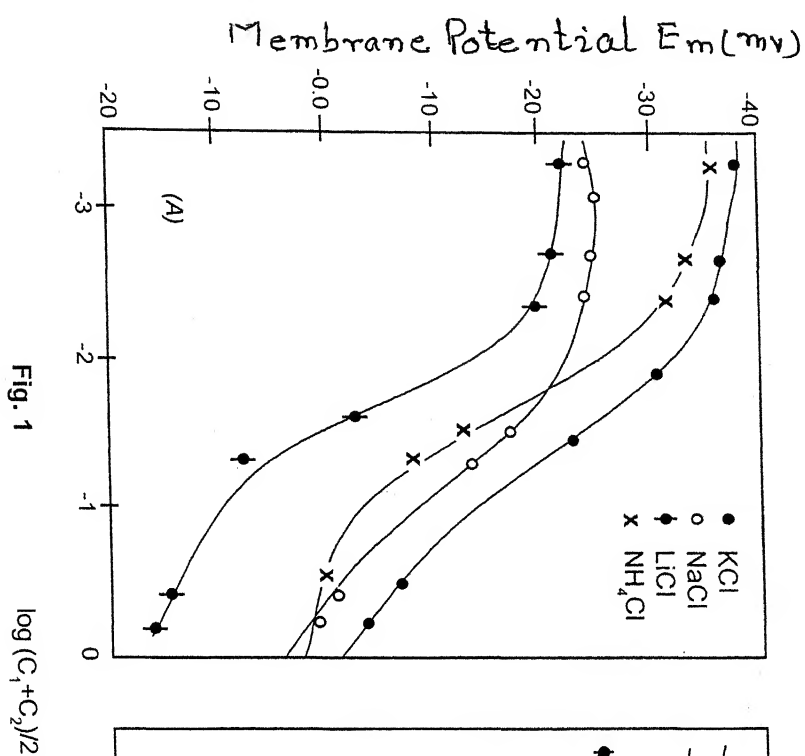
The Values of the Observed Membrane potential E_m (mV) Across Cobalt Sulphide Membrane at $25 \pm 0.1^\circ\text{C}$

Electrolyte Concentration C_2/C_1 (Mol L ⁻¹)	KCl	NaCl	LiCl	NH ₄ Cl
$1/1 \times 10^{-1}$	5.1	0.60	-12.8	0.8
$5 \times 10^{-1}/5 \times 10^{-2}$	7.6	2.7	-11.5	1.2
$1 \times 10^{-1}/1 \times 10^{-2}$	19.3	15.2	-9.2	8.7
$5 \times 10^{-2}/5 \times 10^{-3}$	24.8	18.9	0.1	14.0
$1 \times 10^{-2}/1 \times 10^{-3}$	36.2	24.2	18.9	30.8
$5 \times 10^{-3}/5 \times 10^{-4}$	36.8	24.7	22.5	33.1
$1 \times 10^{-3}/1 \times 10^{-4}$	37.0	25.0	23.8	35.1

Table 2

The Values of the Observed Membrane potential E_m (mV) Across Nickel Sulphide Membrane at $25 \pm 0.1^\circ\text{C}$

Electrolyte Concentration C_2/C_1 (Mol L ⁻¹)	KCl	NaCl	LiCl	NH ₄ Cl
$1/1 \times 10^{-1}$	2.3	-5.3	-11.1	3.8
$5 \times 10^{-1}/5 \times 10^{-2}$	3.3	-3.9	-10.8	5.5
$1 \times 10^{-1}/1 \times 10^{-2}$	20.8	5.5	0.0	14.1
$5 \times 10^{-2}/5 \times 10^{-3}$	22.4	10.7	5.4	18.0
$1 \times 10^{-2}/1 \times 10^{-3}$	31.0	24.9	20.3	30.0
$5 \times 10^{-3}/5 \times 10^{-4}$	37.0	26.4	25.2	34.0
$1 \times 10^{-3}/1 \times 10^{-4}$	37.2	26.5	26.0	34.3



Plots of Membrane Potentials E_m (mv) against $\log (C_1 + C_2)/2$ using 1:1 Electrolytes Across (A) Cobalt Sulphide and (B) Nickel Sulphide Membranes

Parchment supported inorganic precipitate membranes have the ability to generate potentials when they are used to separate electrolyte solutions of different concentrations [24-33]. This property is attributed to the presence of a net charge on the membrane probably due to adsorption of anions or cations. The quantity of charge required to generate potentials, particularly when dilute solutions are used, is small. This, of course, is dependent on the porosity of the membrane. If the membrane pores are too wide, any amount of charge on the membrane does little to generate good potentials. But if the membrane pores are narrow, a little charge on it can produce ideal potentials according to the Nernst-equation.

$$E_m = \frac{RT}{F} \ln a_1 / a_2 \quad [1]$$

Where a_1 and a_2 are the activities of the two solutions on either side of the membrane, E_m is the membrane potential and R , T and F have their usual significance.

An interesting point with the value of E_m for cobalt and nickel sulphide parchment supported membranes is the fact that these are positive when the membrane is separating dilute solutions of the electrolytes [i.e., dilute side C_1 taken as +ve]. This means that the membrane is cation selective, and when the membrane is used to separate concentrated solutions, the values of E_m are -ve, in case of lithium chloride for cobalt sulphide and in sodium chloride and lithium chloride electrolyte solutions for nickel sulphide membrane. Thus the membrane becomes anion selective. Such reversal in selectivity character is not peculiar to these systems [25].

Two important factors, which control electrolyte permeability through a membrane, are charge on the membrane and its porosity. Parchment paper,

except for the presence of some stray and end carboxylic group, contains very few fixed groups. Deposition of inorganic precipitate gives rise to a net negative charge on membrane surface in the dilute solutions of a 1:1 electrolyte leading to the type of ionic distribution associated with the electrical double layer [34]. The stepwise change in membrane potential or the selectivity character or the membrane-electrolyte system may readily be explained in terms of the structural changes produced in the electrical double layer at the interfaces.

The fixed groups present in well-characterized ion exchange membranes can be easily estimated by titration. This procedure was used by Sollner et al. [35] to estimate the end groups and stray carboxylic groups present in the collodion material. Lakshminarayanaiah [36] in his studies with thin membrane of parlodion, used two methods – the isotopic and the potentiometric to evaluate the apparent fixed charge on the membrane material. In the present studies the titration method proved inconvenient and very inaccurate, while the isotopic method was discarded in view of the strong ionic adsorption phenomena exhibited by these systems. Consequently, the potentiometric method was used. This method is based on the fixed charge theory of membrane potential proposed simultaneously by Teorell [2,3], and Meyer and Sievers [37]. The fixed charge concept of Teorell [2,3] and Meyer and Sievers [37] [the TMS theory] for charged membranes is a pertinent starting point for the investigation of the actual mechanisms of the ionic or molecular processes, which occur in the membrane phase. According to this theory, membrane potential is

considered to be composed of two Donnan potential at the two solution membrane interfaces and a diffusion potential arising from unequal concentration of the two membrane phases. These authors derived following equation for membrane potential in millivolts [at 25⁰ C] applicable to a highly idealized system, viz:

$$E_m = 59.2 \left[\log \frac{C_2 \left(\sqrt{4C_1^2 + \bar{X}^2} + \bar{X} \right)}{C_1 \left(\sqrt{4C_2^2 + \bar{X}^2} + \bar{X} \right)} + \bar{U} \log \frac{\left(\sqrt{4C_2^2 + \bar{X}^2} + \bar{X}\bar{U} \right)}{\left(\sqrt{4C_1^2 + \bar{X}^2} + \bar{X}\bar{U} \right)} \right] \quad [2]$$

here $\bar{U} = (\bar{u} - \bar{v}) / (\bar{u} + \bar{v})$, \bar{u} and \bar{v} are the mobilities of cation and anion respectively in the membrane phase; \bar{X} is charge on the membrane expressed in equivalents/liter of imbibed solution. Equation [2] has been frequently used for the evaluation of the fixed charge density \bar{X} of a membrane [38]. In order to evaluate this parameter for the simple case of 1:1 electrolyte and membrane carrying a net negative charge of unity [$\bar{X}=1$], theoretical concentration potentials E_m existing across the membrane are calculated as function C_2 , are given in Table 3. The ratio C_2/C_1 being kept at constant value for different mobility ratios, \bar{u}/\bar{v} . The observed membrane potential values are then plotted in the same graph as a function of $\log [1/C_2]$. The experimental curve is shifted horizontally until it coincides with one of the theoretical curves. The extent of this shift gives $\log \bar{X}$ and the coinciding theoretical curve, the value of \bar{u}/\bar{v} , Figs. [3 and 4]. In the case of cobalt and nickel sulphide membranes the observed membrane potential

TABLE-3

Theoretical Values of Membranes E_m [mv] Calculated From Teorell-Meyer-Seivers Method For Different Mobility Ratio \bar{u}/\bar{v} and ($\bar{x}=1$) At Different Concentrations.

Mobility ratio \bar{u}/\bar{v} Concentration C_2/C_1 [Mol/l]	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
$1 \times 10^{-1}/1$	-35.0	-22.5	-3.0	8.3	15.3	16.1	20.2	23.5
$5/5 \times 10^{-1}$	-22.5	10.0	25.0	30.8	40.7	20.1	30.2	30.0
$1/1 \times 10^{-1}$	15.0	30.0	45.2	46.0	45.0	34.0	37.5	45.2
$5 \times 10^{-1}/1 \times 10^{-2}$	35.0	40.0	47.5	47.2	50.2	50.0	53.0	55.0
$1 \times 10^{-1}/1 \times 10^{-2}$	50.0	50.0	50.0	55.5	55.0	55.0	57.0	58.8
$5 \times 10^{-1}/1 \times 10^{-2}$	58.0	57.0	55.0	58.0	59.0	59.2	59.4	60.0
$1 \times 10^{-1}/1 \times 10^{-2}$	59.0	59.0	59.0	59.0	59.9	59.9	60.0	60.0
$5 \times 10^{-1}/1 \times 10^{-2}$	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
$1 \times 10^{-1}/1 \times 10^{-2}$	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0

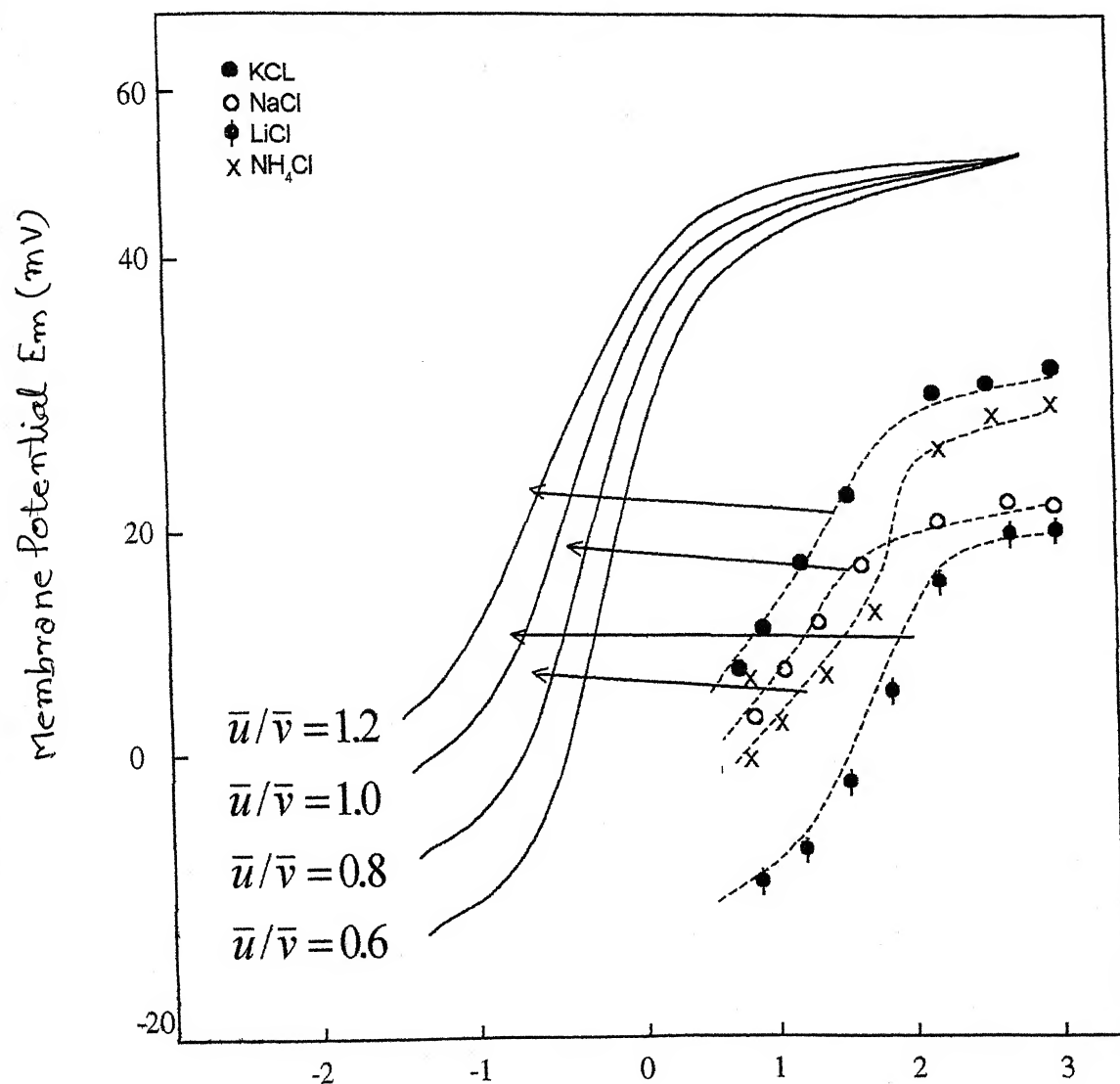


FIG. - 3

Evaluation of membrane fixed charge density (\bar{x}) and mobility ratio (\bar{U}/\bar{V}) in the membrane phase.

Smooth curves are theoretical concentration potentials for a cation selective membrane ($\bar{x} = 1$) at different mobility ratios \bar{U}/\bar{V} . Experimental values for cobalt sulphide membrane are shown by the broken lines, See Text

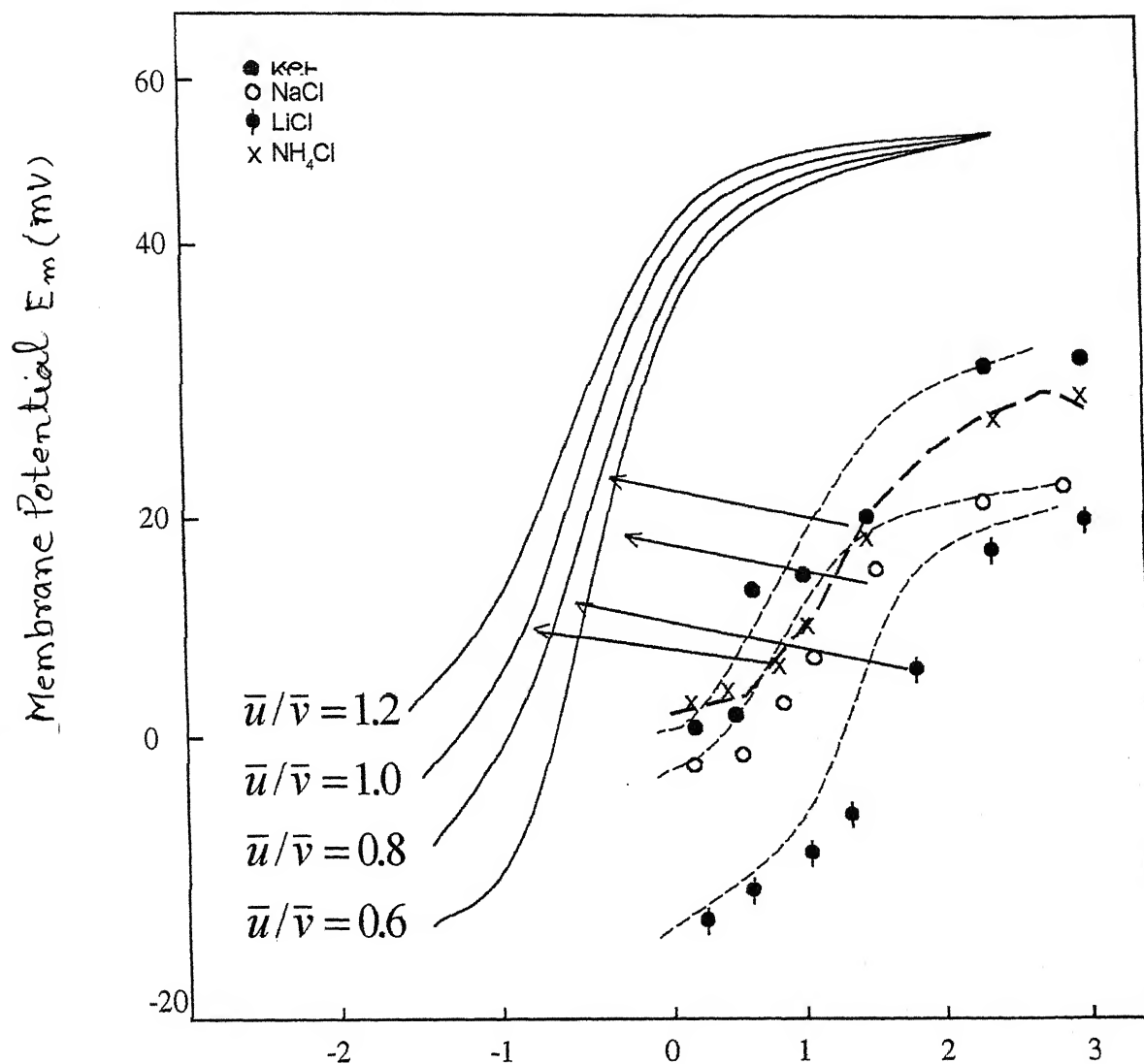


FIG. - 4

Evaluation of membrane fixed charge density (\bar{x}) and mobility ratio (\bar{U}/\bar{V}) in the membrane phase.

Smooth curves are theoretical concentration potentials for a cation selective membrane ($\bar{x} = 1$) at different mobility ratios \bar{U}/\bar{V} . Experimental values for nickel sulphide membrane are shown by the broken lines, See Text

curves on shifting horizontally did not overlap with any of the theoretical curves particularly in the dilute ranges. As a result eq. [2] was used in another way, in the way Teorell did, to evaluate \bar{X} . A family of theoretical curves [Figs. 3 and 4] were constructed assigning $\bar{X} = 1$ and successively decreasing values to \bar{X} [$\bar{X} < 1$] keeping $\bar{u}/\bar{v} = 0.2$ [Table 5]. The curves thus obtained have same shape and limit but are transposed along the $\log C_2$ axis. The value of \bar{X} is then given by the curve with which the experimental curve coincided. The values thus derived are given in Table 4. In addition to the value of \bar{X} , the plotting in this form correctly predicts diffusion potential at the limit $\bar{X} = 0$. The diffusion potential values derived in this way were found to have approximately the same magnitude and sign as the potential across the membranes when these are used to separate highly concentrated solutions of an electrolyte [Table 4]. In view of this limiting diffusion potential value, the variation in membrane potential across cobalt and nickel sulphide membranes with the change in external electrolyte concentrations may be ascribed to be due to the structural changes produced in the electrical double layer at the membrane-solution interfaces. Thus cobalt and nickel sulphide membrane electrolyte systems may be more conveniently described as consisting of two mini cells – one with constant e.m.f. corresponding to the limiting diffusion potential and the other with variable e.m.f. representing the internal potential difference [0 to 60 mV approximately]. Since the total membrane potential changes sign as the concentration of the electrolytes across the membranes are changed, thus it may be concluded that these mini cells are combined together in series but

TABLE-4

Values of Membrane Charge Density X [eq/L], Mobility Ratio $[U/V]$ And Diffusion Potential [mv] For Various Membrane Electrolyte System Using Teorell-Meyer-Sievers Theory At $25 \pm 0.1^\circ\text{C}$

Electrolyte		KCl	NaCl	LiCl	NH ₄ Cl
Membranes	Parameters				
Cobalt sulphide	$[X] \times 10^3$	1.4	1.7	2.7	2.2
	$[u/v]$	0.2	0.2	0.2	0.2
	[Diff. Pot.]	5.1	0.6	-12.8	0.8
Nickel sulphide	$[X] \times 10^3$	1.6	1.2	1.5	1.5
	$[u/v]$	0.2	0.2	0.2	0.2
	[Diff. Pot.]	2.3	-5.3	-11.1	3.8

TABLE-5

Theoretical Values of Membranes E_m [mv] Calculated From Teorell-Meyer-Seivers Method For Different Values of \bar{X} and $\bar{u}/\bar{v} = 0.2$.

Charge Density $[\bar{X}]$ Concentration C_2/C_1 [Mol/l]	0.1	0.01	0.005	0.001	0.0007	0.0005	0.0001
$1 \times 10^{-1}/1$	-39.1	-39.5	-39.1	-39.1	-39.1	-39.8	-39.1
$5/5 \times 10^{-1}$	-39.1	-39.7	-39.1	-39.1	-39.1	-39.8	-39.1
$1/1 \times 10^{-1}$	-21.9	-37.3	-38.2	-38.2	-39.0	-39.0	-39.0
$5 \times 10^{-1}/1 \times 10^{-2}$	-8.1	-36.4	-36.8	-36.2	-37.8	-39.0	-39.1
$1 \times 10^{-1}/1 \times 10^{-2}$	31.1	-30.7	-33.7	-35.2	-34.8	-37.5	-38.0
$5 \times 10^{-1}/1 \times 10^{-2}$	50.3	-2.2	-10.5	-30.7	-24.3	-28.5	-37.4
$1 \times 10^{-1}/1 \times 10^{-2}$	59.2	21.5	21.8	10.5	-10.0	-22.0	-30.0
$5 \times 10^{-1}/1 \times 10^{-2}$	59.5	41.3	54.7	21.9	9.1	-20.0	26.9
$1 \times 10^{-1}/1 \times 10^{-2}$	59.5	59.5	58.0	24.5	15.2	-19.5	-25.5

operating in opposite direction and that the membrane solution interface seems to be the rate determining step as suggested by Tien and Ting [39] for bilayer membranes.

Kobatake et al. [12] on the basis of the thermodynamics of irreversible processes derived the following equation for the electrical potential E_m which arises when a negatively charged membrane separates two solutions of a 1:1 electrolyte of concentrations C_1 and C_2 [$C_1 < C_2$]:

$$E_m = - \frac{RT}{F} \left[\frac{1}{\beta} \ln \frac{C_2}{C_1} - \left(1 + \frac{1}{\beta} - 2\alpha \right) \ln \left(\frac{C_2 + \alpha\beta \bar{X}}{C_1 + \alpha\beta \bar{X}} \right) \right] \quad [3]$$

Where $\alpha = U / [u + v]$

$$\beta = 1 + KF \bar{X} / u$$

F and K represent, respectively, the Faraday constant and a constant dependent upon the viscosity of the solution and structural details of the polymer network of which the membrane is composed. To evaluate the membrane parameters, α , β and \bar{X} , two limiting forms of the above equation were derived. When the external salt concentration C is sufficiently small,

$$|E_m^\sigma| = \frac{1}{\beta} \ln \gamma - \left(\frac{\gamma - 1}{\alpha\beta\gamma} \right) \left(1 + \frac{1}{\beta} - 2\alpha \right) \left(\frac{C_2}{\bar{X}} \right) + \dots \quad [4]$$

$$\text{where } |E_m^\sigma| = FE_m / RT$$

$$\text{and } \gamma = C_2 / C_1$$

when the salt concentration C is high,

$$\frac{1}{t_-} = \frac{1}{1-\alpha} + \frac{(1 + \beta - 2\alpha\beta)(\gamma - 1)\alpha}{2(1-\alpha)^2 \ln \gamma} \left(\frac{\bar{X}}{C_2} \right) + \dots \quad [5]$$

where t_- is the apparent transference number of anions in a negatively charged membrane defined by

$$E_m = [1 - 2t_-] \ln \gamma \quad [6]$$

The value of t_- calculated from observed membrane potentials using eq. [6] for cobalt and nickel sulphide membranes, are given in Tables 6 and 7. Equation [4] was used to give the value of β [see Table 8] and a relation between α and \bar{X} by evaluating the intercept and the initial slope of the plot of E_m against C_2 [Figs. 5 and 6], while eq. [5] was used to evaluate α [see Table 8] from the intercept of a plot of $1/t_-$ against $1/C_2$ [Figs. 7 and 8]. The values of \bar{X} were determined by inserting this value of α in the relation between α and \bar{X} obtained earlier. The values of \bar{X} derived in this way for the membranes and 1:1 electrolytes are given in Table 9.

Once the values of the parameters α , β and \bar{X} for a given membrane-electrolyte system have been determined one can get the theoretical E_m Vs. C_2 curve using eq. [3] for any given γ [$=C_2/C_1$] and compare it with the corresponding experimental data. For this comparison

TABLE-6

Transference Number [t_-] of Coins From Observed Membrane Potential At Various Electrolyte Concentration Through Cobalt Sulphide Membrane

Electrolyte	KCl	NaCl	LiCl
Concentration C_2/C_1 [mol/l]			
$1 \times 10^{-1}/1 \times 10^{-2}$	0.68	0.72	0.71
$5 \times 10^{-2}/5 \times 10^{-3}$	0.65	0.70	0.66
$1 \times 10^{-2}/1 \times 10^{-3}$	0.64	0.58	0.53
$5 \times 10^{-3}/5 \times 10^{-4}$	0.50	0.52	0.48
$1 \times 10^{-3}/1 \times 10^{-4}$	0.39	0.44	0.35
$5 \times 10^{-4}/5 \times 10^{-5}$	0.32	0.31	0.27
$1 \times 10^{-4}/1 \times 10^{-5}$	0.31	0.27	0.33

TABLE-7

Transference Number t_- of Coins From Observed Membrane Potential At Various Electrolyte Concentration Through Nickel Sulphide Membrane

Electrolyte	KCl	NaCl	LiCl
Concentration C_2/C_1 [mol/l]			
$1 \times 10^{-1}/1 \times 10^{-2}$	0.75	0.75	0.74
$5 \times 10^{-2}/5 \times 10^{-3}$	0.73	0.74	0.72
$1 \times 10^{-2}/1 \times 10^{-3}$	0.66	0.60	0.66
$5 \times 10^{-3}/5 \times 10^{-4}$	0.52	0.50	0.44
$1 \times 10^{-3}/1 \times 10^{-4}$	0.36	0.32	0.36
$5 \times 10^{-4}/5 \times 10^{-5}$	0.31	0.31	0.33
$1 \times 10^{-4}/1 \times 10^{-5}$	0.29	0.24	0.27

TABLE-8

Values of the Membrane Parameter α and β for Various Membrane Electrolyte At $\gamma = 10$

Electrolyte Membranes	KCl		NaCl		LiCl		NH ₄ Cl	
	α	β	α	β	α	β	α	β
Cobalt Sulphide	0.18	1.2	0.17	1.2	0.16	1.2	1.6	1.4
Nickel Sulphide	0.11	1.5	0.13	1.5	0.14	1.5	1.2	1.5

TABLE-9

Values of The Effective Fixed Charge Density \bar{X} [eq/l] Using Kobatake's Method For Various Membrane Electrolyte System At $25 \pm 0.1^\circ\text{C}$

Electrolyte Membranes	KCl	NaCl	LiCl	NH ₄ Cl
Cobalt sulphide [\bar{X}] x 10 ³ , eq/l	3.8	1.3	2.1	3.2
Nickel sulphide [\bar{X}] x 10 ³ , eq/l	2.7	2.5	2.9	2.5

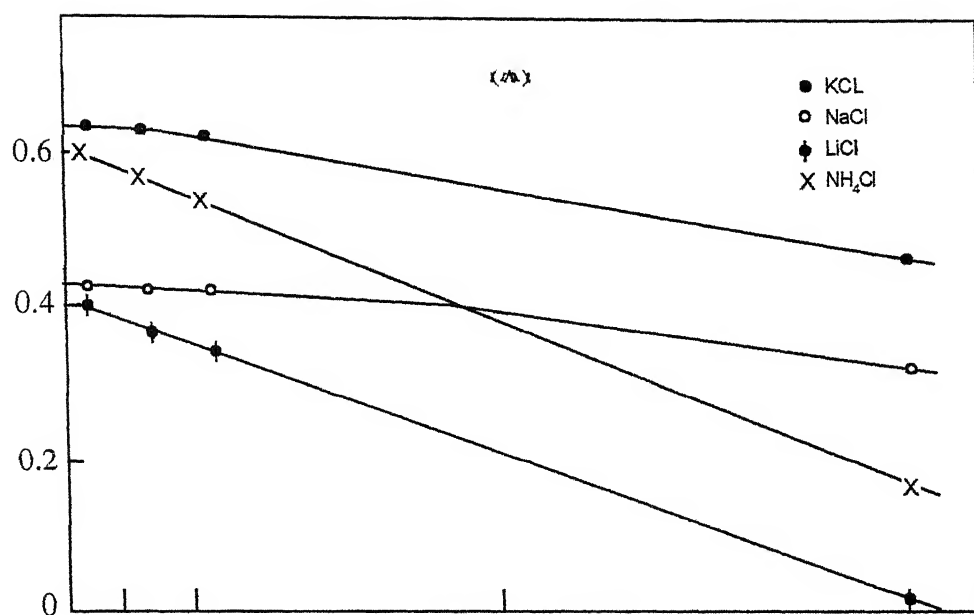


FIG. - 5

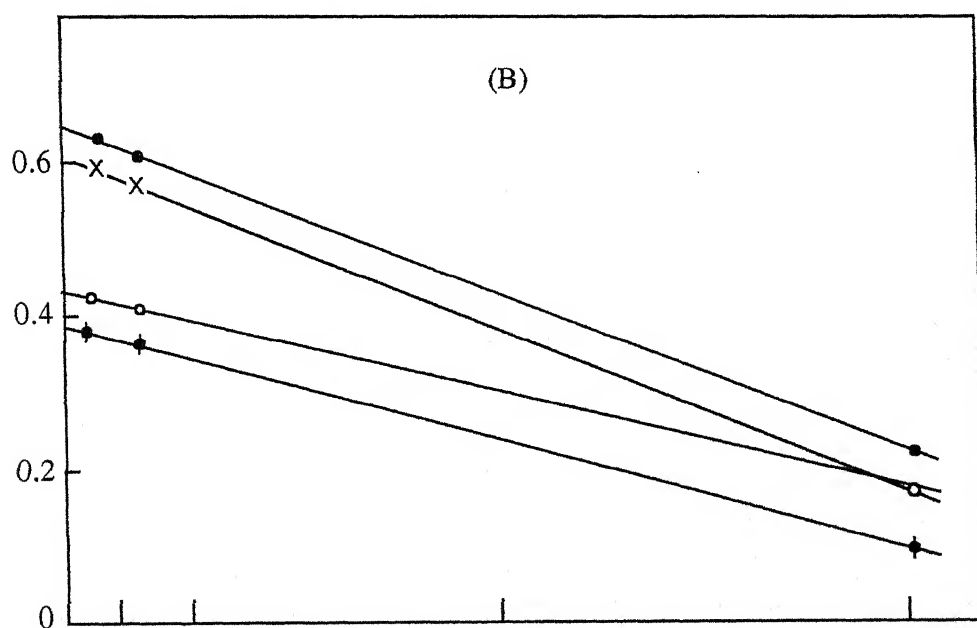


FIG. - 6

Plots of $|E_m^0|/2.303$ against C_2 for (A) cobalt sulphide and (B) nickel sulphide membranes.
 In contact with various 1:1 electrolyte solutions

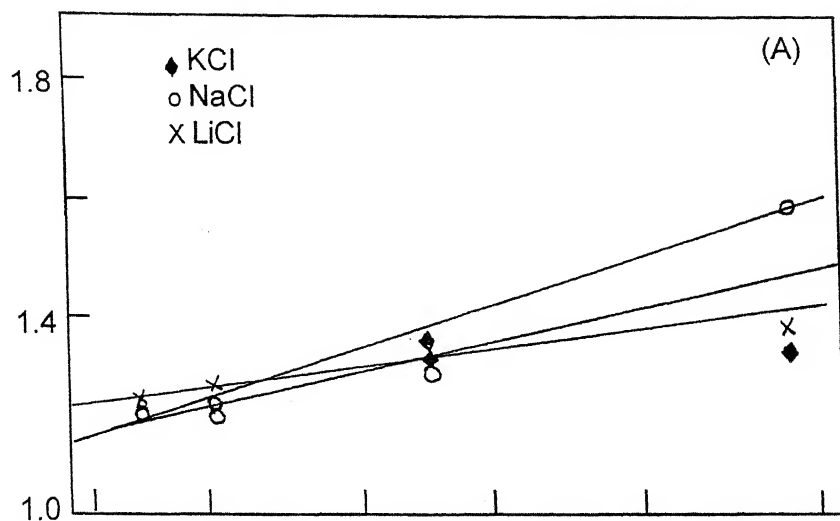


FIG. - 7

$1/t$

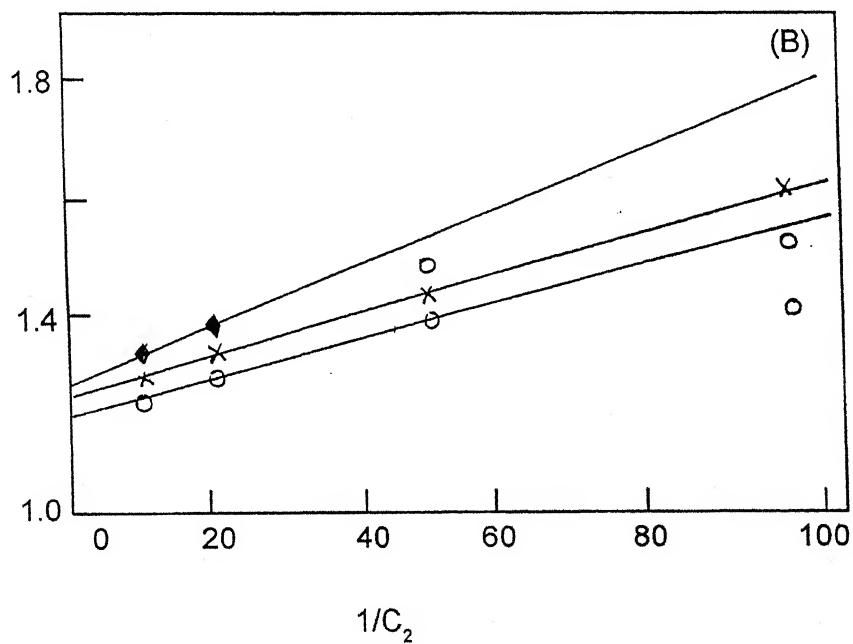


FIG. - 8

PLOTS OF $1/t$ AGAINST $1/C_2$ FOR (A) COBALT SULPHIDE AND (B) NICKEL SULPHIDE MEMBRANES USING 1:1 ELECTROLYTE SOLUTIONS AT CONSTANT γ ($\gamma = 10$)

eq. [3] can be rewritten in the following form as suggested by Kobatake and coworkers [12].

$$\frac{(\gamma - e^q)}{(e^q - 1)} = Z \quad [7]$$

with q and Z defined by

$$q = \frac{|E_m^-| + (1 - 2\alpha) \ln \gamma}{1/\beta + (1 - 2\alpha)}$$

and $Z = C_2 / \alpha\beta\bar{X}$. Thus if eq. [7] is valid the value of $[\gamma - e^q]/[e^q - 1]$ calculated from the measured E_m with predetermined α , β and \bar{X} and the given value of γ must fall on a straight line which has a unit slop and passes the co-ordinate origin when plotted against Z . ^{Fig. 9 and 10.} This behavior should be observed irrespective of the value of γ and the kind of membrane-electrolyte system used.

Recently Kobatake and Kamo [17] derived another equation eq. [8] for the membrane potential starting with the basic flow equation provided by the thermodynamics of irreversible processes and using a different set of assumptions: namely, [a] the contribution of mass movement is negligible [17], and [b] small ions do not behave ideally in a charged membrane [17]. Their result is:

$$E_m = -\frac{RT}{F} \left[\ln \frac{C_2}{C_1} + (2\alpha - 1) \ln \frac{\sqrt{4C_2^2 + \phi^2 X^2} + (2\alpha -)\phi X}{\sqrt{4C_1^2 + \phi^2 X^2} + (2\alpha -)\phi X} - \ln \frac{\sqrt{4C_2^2 + \phi^2 X^2} + \phi X}{\sqrt{4C_1^2 + \phi^2 X^2} + \phi X} \right] \quad [8]$$

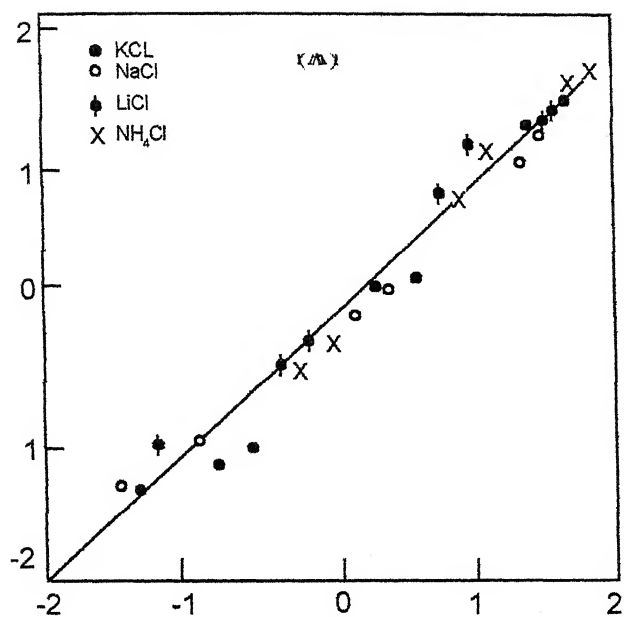


FIG. 9

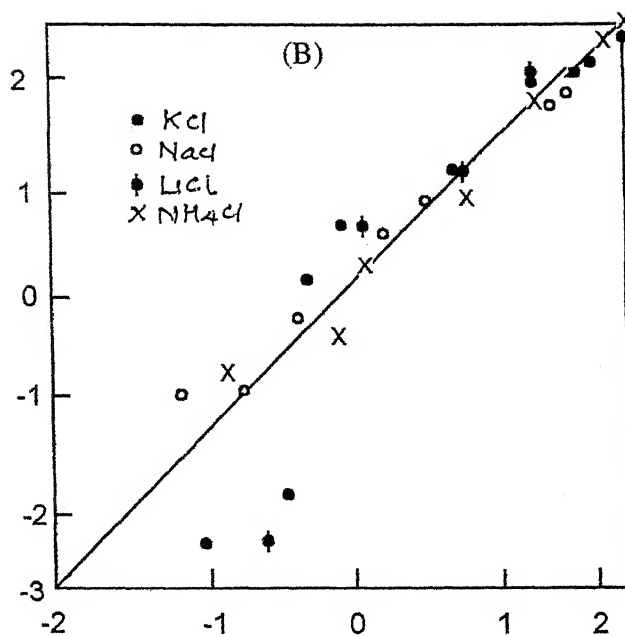


FIG. 10

FIG. - 9

Plots of $\log (r-e^a)/(e^a-1)$ against $\log Z$ for (A) Cobalt sulphide and (B) nickel sulphide membrane in contact with various 1:1 electrolytes

where ϕ is a characteristic factor of the membrane- electrolyte pair, and represents the fraction of counter ions not tightly bound to the membrane skeleton. The product ϕX is termed the thermodynamically effective fixed charge density of a membrane; the other terms have their usual significance. Equation [8] reduces to the TMS membrane potential for $\phi = 1$. Since it is somewhat troublesome to evaluate ϕX at an arbitrary external electrolyte concentration from the observed membrane potential using eq. [8], Kobatake and Kamo [17] have proposed a simple method using the following approximate equation for the diffusive contribution to the e.m.f. of a cell with transport:

$$E_m = - \frac{RT}{F} (1 - 2t_{app}) \ln (C_2 / C_1) \quad [9]$$

where t_{app} is the apparent transference number of ions in the membrane phase. Comparison of eqs. [8] and [9] gives

$$t_{app} = \frac{1 - 2\alpha}{2} \frac{\ln \left(\frac{\sqrt{4\xi_2^2 + 1 + 2\alpha} - 1}{\sqrt{4\xi_1^2 + 1 + 2\alpha} - 1} \right)}{\ln \gamma} + \frac{\ln \left(\frac{\sqrt{4\xi_2^2 + 1 + 1}}{\sqrt{4\xi_1^2 + 1 + 1}} \right)}{2 \ln \gamma} \quad [10]$$

where $\xi = C / \phi X$

on the other hand [16,17], the mass fixed transference number of coins in a negatively charged membrane immersed in an electrolyte solution of concentration C was defined by

$$t_- = v \bar{C}_- / (u \bar{C}_+ + v \bar{C}_-) \quad [11]$$

where \bar{C}_+ and \bar{C}_- are the concentrations of cation and anion, respectively, in the membrane phase. This equation was transformed to

$$t_- = 1 - \alpha \frac{\sqrt{4\xi^2 + 1} + 1}{\sqrt{4\xi^2 + 1} + (2\alpha - 1)} \quad [12]$$

using certain equations for the activity coefficients, mobilities of small ions in the membrane phase, and the equilibrium condition for electrical neutrality [16,17]. The difference between the apparent transference number t_{app} calculated from eq. [10] and t_- from eq. [12] for various reduced concentrations ξ [$\xi = C/\phi X$] was found to be always less than 2% over a wide range of external electrolyte concentrations. Therefore, t_{app} and t_- were considered practically the same. As a result, the apparent transference number evaluated from the membrane potential data used for the determination of the thermodynamically effective fixed charge density ϕX of the membrane at a given average salt concentration C [$C = [C_1 + C_2]/2$] using eq. [12] At the same time rearrangement of eq. [12] provides a definition of perm selectivity P_s , given by the expression

$$\frac{1}{(4\xi^2 + 1)^{1/2}} = \frac{1 - t_- - \alpha}{\alpha - (2\alpha - 1)(1 - t_-)} = P_s \quad [13]$$

This equation can be used to find the perm selectivity from membrane potential measurements using eq. [9] If the transport number of coins [$t_{\text{or}} t_{\text{app}}$] is zero, the membrane is perfectly selective and $P_s=1$, while if the transport number of coins has the value in free solution $P_s=0$. The values of P_s obtained in Tables [10 and 11] using the right hand side of eq. [13] were plotted against $\log C$. The concentration at which P_s [where $\xi = C/\phi X = 1$] becomes $[1/5]^{1/2}$ gives the value of the thermodynamically effect fixed charge density ϕX as required by the left side of eq. [13]. Figures 11 and 12 represent plots of P_s versus $\log C_1+C_2/2$ for the parchment supported cobalt and nickel sulphide membranes in contact with various 1:1 electrolytes. The value of ϕX thus derived for the membranes and 1:1 electrolyte combinations are given in Table 12.

More recently. Tasaka et al. [21] derived an equation for the membrane potential existing across a charged membrane. The total membrane potential E_m was considered as the sum of a diffusion potential E_d inside the membrane and the electrostatic potential differences E_e between the membrane surfaces and the electrolyte solutions on both sides of the membrane. The diffusion potential E_d was obtained by integrating the basic flow equation for diffusion [39], while the electrostatic potential difference was calculated from the Donnan's theory. Stated mathematically,

$$E_m = E_d + E_e \quad [14a]$$

where

Table 10

Values of permselectivity P_s of the Cobalt Sulphide membrane using various 1:1 electrolytes at different concentration for cobalt sulphide membrane.

Electrolyte Concentration C_2/C_1 (Mol L ⁻¹)	KCl	NaCl	LiCl	NH ₄ Cl
1/1 x 10 ⁻¹	0.08	0.22	0.06	0.02
5x10 ⁻¹ /5x10 ⁻²	0.12	0.26	0.17	0.04
1x10 ⁻¹ /1x10 ⁻²	0.32	0.45	0.21	0.14
5x10 ⁻² /5x10 ⁻³	0.42	0.50	0.34	0.24
1x10 ⁻² /1x10 ⁻³	0.60	0.57	0.60	0.52
5x10 ⁻³ /5x10 ⁻⁴	0.62	0.58	0.64	0.56
1x10 ⁻³ /1x10 ⁻⁴	0.64	0.60	0.66	0.60

Table 11

Values of permselectivity P_s of the Nickel Sulphide membrane using various 1:1 electrolytes at different concentration for Nickel Sulphide membrane.

Electrolyte Concentration C_2/C_1 (Mol L ⁻¹)	KCl	NaCl	LiCl	NH ₄ Cl
1/1 x 10 ⁻¹	0.04	0.12	0.17	0.08
5x10 ⁻¹ /5x10 ⁻²	0.06	0.14	0.18	0.10
1x10 ⁻¹ /1x10 ⁻²	0.36	0.30	0.34	0.24
5x10 ⁻² /5x10 ⁻³	0.38	0.38	0.42	0.32
1x10 ⁻² /1x10 ⁻³	0.52	0.55	0.50	0.52
5x10 ⁻³ /5x10 ⁻⁴	0.62	0.59	0.66	0.58
1x10 ⁻³ /1x10 ⁻⁴	0.62	0.61	0.68	0.62

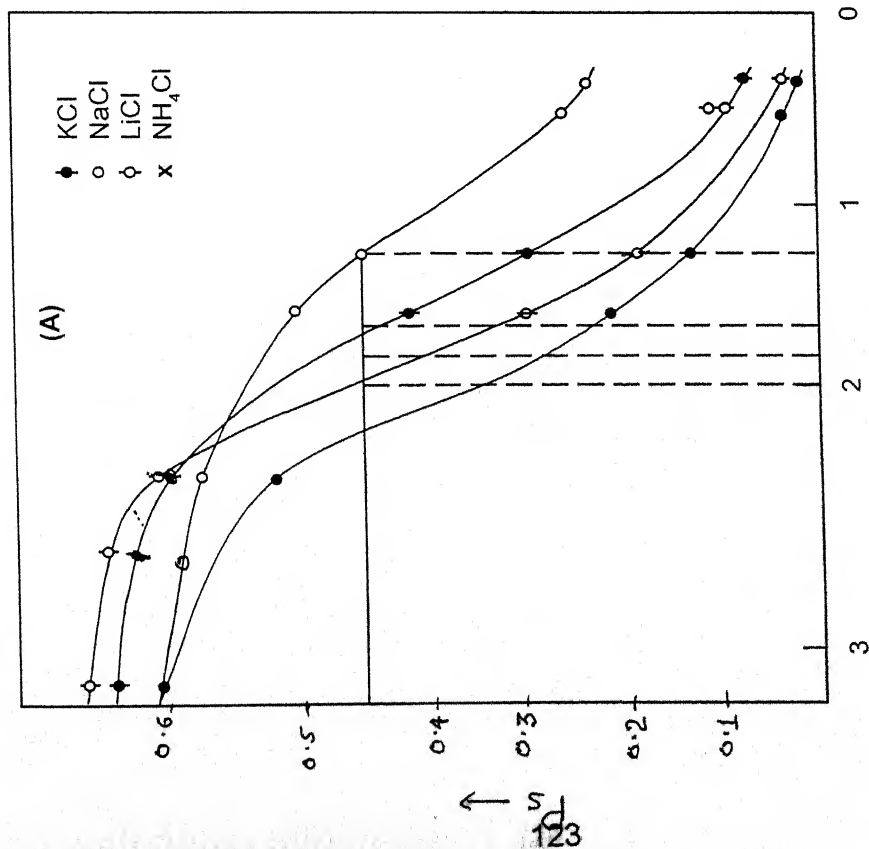


Fig.-11

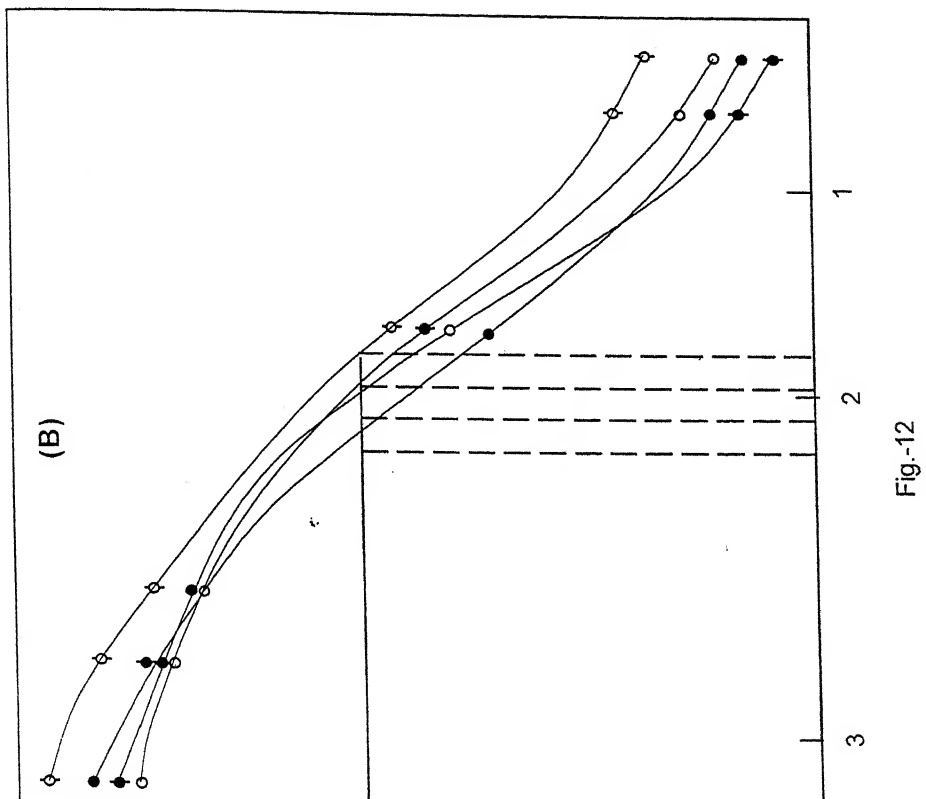


Fig.-12

Plots of P_s Against $-\log (C_1 + C_2)/2$ for (A) Cobalt Sulphide And (B) Nickel Sulphide membranes

TABLE-12

Values of Effective Fixed Charge Density ϕX [eq/l] Obtained From Kobatake's Perm-selectivity Method For Various Membrane Electrolyte Systems At $25 \pm 0.1^\circ\text{C}$

Electrolyte Membranes	KCl	NaCl	LiCl
Cobalt sulphide [ϕX] $\times 10^3$, eq/l	3.5	2.2	2.2
Nickel sulphide [ϕX] $\times 10^3$, eq/l	2.2	2.2	2.2

TABLE-13

Values Of Effective Fixed Charge Density ϕX [eq/l] Obtained From Tasaka's Method For Various Membrane Electrolyte System At $25 \pm 0.1^\circ\text{C}$

Electrolyte Membranes	KCl	NaCl	LiCl
Cobalt sulphide [ϕX] $\times 10^3$, eq/l	0.1	0.07	1.0
Nickel sulphide [ϕX] $\times 10^3$, eq/l	0.1	1.0	1.2

$$\begin{aligned}
-E_d = & - \int_1^2 \frac{J_0}{F \bar{C}_0} \frac{\phi X}{(\bar{C}_- + \phi X) u + \bar{C}_- v} dx + \\
& \frac{RT}{F} \int_1^2 \frac{(\bar{C}_- + \phi X) u}{(\bar{C}_- + \phi X) u + \bar{C}_- v} d \ln \bar{a}_+ - \\
& \frac{RT}{F} \int_1^2 \frac{\bar{C}_- v}{(\bar{C}_- + \phi X) u + \bar{C}_- v} d \ln \bar{a}_-
\end{aligned} \quad [14b]$$

and

$$-E_e = - \frac{RT}{F} \ln \left(\frac{\bar{a}_1 a_2}{a_1 a_2} \right) \quad [14c]$$

where a_1 and a_2 are the activities of the electrolytes on the two sides of the membrane, the overbar refers to the phenomena in the membrane phase. J_0 is the flow of electrolyte in the absence of an external electrolyte field, the other symbol have their usual significance. On integrating eq. [14] in the limit of high electrolyte concentrations across the membrane, one obtains the following equation for the membrane potential:

$$\begin{aligned}
-E_m = & \frac{RT}{F} \left(\frac{\phi X}{2} \right) \left(\frac{\gamma - 1}{\gamma} \right) \frac{1}{C_2} + \frac{RT}{F} \left(\frac{u - v}{u + v} \right) \left[\frac{1 - \frac{\phi X J_0}{RT \bar{C}_0 (u - v) K}}{1 - \frac{\phi X J_0}{2RT \bar{C}_0 v K}} \right] \ln \gamma \\
& + \frac{RT \phi X}{2Fuv} \left(\frac{J_0}{RT \bar{C}_0 K} \right)^2 \frac{\left[1 - \frac{\phi X J_0 (u + v)}{4RT \bar{C}_0 uv K} \right]}{\left(1 - \frac{\phi X J_0}{2RT \bar{C}_0 v K} \right)^2} (\gamma - 1) C_2
\end{aligned} \quad [15]$$

At high electrolyte concentrations, eq. [15] can be approximated by

$$-E_m = \frac{RT}{F} \frac{(\gamma - 1)}{\gamma} \left(\frac{\phi X}{2} \right) 1/C_2 + \dots \quad [16]$$

Equation [16] predicts a linear relationship between E_m and $1/C_2$ from which ϕX can be calculated. Plots of E_m versus $1/C_2$ for the membranes are represented in Figs. 13 and 14. Sets of straight lines in agreement with eq. [16] are obtained. The values of ϕX derived from the slopes of the lines are given in Table 13.

It is noted from Tables 5, 9, 12 and 13 that the charge densities of the membrane electrolyte system are low. This is in accordance with our earlier findings of diffusion rate studies. Further, the values derived from different methods are almost the same. A little difference may be attributed to the different procedures adopted. It is concluded, therefore, that the methods developed recently by Kobatake et al. and Tasaka et al. for the evaluation of effective fixed charge density are valid for the systems under investigation.

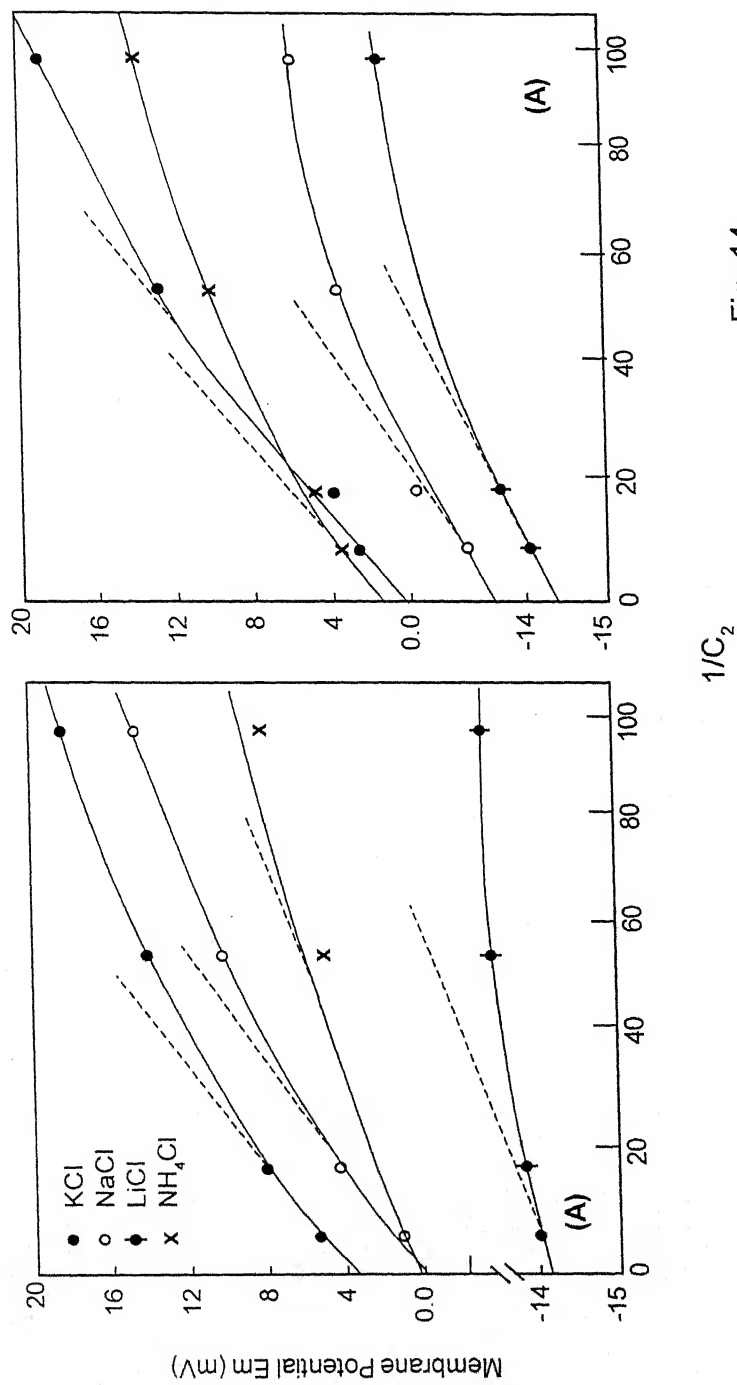


Fig.-13
Plots of Membrane Potential E_m (mV) against $1/C_2$ for (A) CoBALT Sulphide
and (B) Nickel Sulphide Membranes

Fig.-14

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CHAPTER 3

MEMBRANE SELECTIVITY

INTRODUCTION

When two electrolytic solutions having different concentrations are separated by a membrane, the mobile species penetrate the membrane and various transport phenomena are induced in the system [1]. The total electric potential difference observed under zero current flow between two aqueous solutions separated by a membrane has been one of the most widely characterized electrochemical and bioelectric phenomena [2-8]. The fixed charge concept of Teorell [9] and Meyer and Sievers [10] for the charged membranes is a pertinent starting point for the investigation of actual mechanisms of ionic or molecular processes which occur in the membrane phase. For biological membranes the electrical potential difference is usually described in terms of Goldman - Hodgkin Katz [11,12] equation, whereas for certain ion exchange membranes permeable solely to species of one sign, is described by generalized Nernst equation. Both the Goldman-Hodgkin-Katz and Nernst equations contain ionic permeability ratio terms. Depending on the transport mechanism or the assumptions made in the derivations, the permeability ratio has been given various physical meanings as : mobility ratio [13], ion exchange equilibrium constant [14], the product of the mobility ratio and the Donnan ratio [9, 10], the product of the mobility ratio and the distribution coefficient ratio [12], the product of the mobility ratio and ion exchange equilibrium constant [15,16] or the product of the equivalent conductance ratio and the ratio of partition coefficient [2]. Sandblom et al. [2,3,17] have discussed the significance and implications of the observed permeability ratio.

Today, separation membranes have become essential materials not only in industries, but also in daily human life. Thus, various membranes of peculiar nature have been developed : membranes for reverse osmosis, nanofiltration, microfiltration, pervaporation processes, ion exchange membranes, membranes for medical use such as an artificial kidney, etc [18]. Among these membranes, ion exchange membranes are one of the most advanced separation membranes. Basically, the ion exchange membranes separate cations from anions and anions from cations. As a result of extensive studies, the separation between cation and anion has attained almost an ideal level in any concentration of solution. The ion exchange membranes have been mostly used in the solutions containing multi components, such as electrodialytic concentration of sea water to produce sodium chloride, demineralization of saline water, desalination of cheese whey solutions etc. Perm selectivity among components in a mixture through non porous separation membranes is governed by the difference of the affinity of respective component with the membrane and the difference of the migration speed of the component in the membrane phase. Therefore, ion-exchange membranes have perm selectivity for specific ions like, monovalent ion perm selective ion exchange membranes [19, 20], proton perm selective ion exchange membranes [21] etc., have been used industrially. Recently a number of reviews have been appeared dealing the ion selectivity of membranes [22, 23-29].

In this chapter the author has confined the work upto the study of the selectivity of metal ions of both the nickel and cobalt sulphide membranes.

In order to evaluate the selectivity values of the metal ions in the membrane phase, the measurements of electrical membranes potential, biionic and multi-ionic potential have experimentally been carried out. The values of membrane conductance also contribute in the evaluation of these results. Different methods with individual membrane theories based on the principles of non-equilibrium thermodynamics have been used for the evaluation of thermodynamically effective fixed charge density, permeability ratio of cations using conductivity measurements and potentiometric selectivity constant of the parchment supported nickel and cobalt sulphide membranes using experimentally observed values to confirm the findings.

The theory of absolute reaction rates has also been utilized for the evaluation of Arrhenius activation energy [E_a], the change of enthalpy [ΔH^*], entropy [ΔS^*] and free energy [ΔF^*] of activation by making the use of conductance data observed for membrane in contact with various monovalent electrolytes. On the basis of the magnitude of these thermodynamic activation parameters, the selective membrane behaviour has also been discussed in the light of an advanced theory of membrane selectivity [30].

EXPERIMENTAL

Parchment supported membranes of nickel and cobalt sulphide respectively were prepared by the method of interaction suggested by kushwaha et al. [4] with the help of nickel [II] chloride, cobalt [II] chloride, sodium sulphide and parchment paper.

Actually the precipitate formation of nickel and cobalt sulphide takes place in the interstices of the parchment paper by the method of interaction. Thus parchment paper and inorganic precipitate as a whole act as a membrane. The membranes thus prepared were washed with deionized water to remove free electrolytes.

The biionic and multiionic potentials across freshly prepared parchment supported nickel and cobalt sulphide membranes were measured by constructing an electrochemical cell of the following type and using a Pye-precision vernier potentiometer.

Reference	Electrolyte	Membrane	Electrolyte	Reference
electrode	Solution [I]		Solution [II]	electrode

The reference electrodes used were reversible saturated calomel electrode $[\text{Hg} / \text{Hg}_2 \text{Cl}_2]$ connected to the solutions via. KCl-agar bridges. Membrane potentials were measured by maintaining a tenfold difference in the electrolyte concentrations. The biionic potential [BIP] measurements were carried out either by keeping the concentration of both the electrolytes

same on the two sides of the membrane, or by maintaining the concentration of one of the electrolytes constant and changing that of the other. Multiionic potentials were measured on the lines suggested by Lakshminarayanaiah [31].

For the measurement of electrical conductivity, membrane was first dipped and equilibrated in an appropriate electrolyte solution. It was then clamped between two half cells and measurements were made according to Fig.-1, using a conductivity bridge [Cambridge Instrument Co. Ltd., England]. All measurements were carried out at 25 ± 0.1 °C. The error in measurement of membrane potentials was within ± 0.1 % whereas electrical conductivity could be measured to better than 0.05%.

RESULTS AND DISCUSSION

The values of membrane potential observed experimentally across both inorganic precipitate parchment supported nickel and cobalt sulphide membranes by taking dilute solution side positive are given in Tables- 1 and 2 respectively. The variation of membrane potential with the change of electrolyte concentrations for various 1: 1 electrolytes is shown in Figs.-2 and 3. In both the figures it has been found that membrane potential values decrease with the increase of electrolyte concentration and thus on the basis of these potential values, membranes follow the sequence of the selectivity of metal ions:

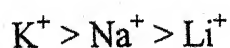


Table 1

The values of the observed membrane potential E_m [mV] across nickel sulphide membrane at $25 \pm 0.1^\circ\text{C}$

Electrolyte Concentration / Mol L ⁻¹ C_{II}/C_I	KCl	NaCl	LiCl
$1 \times 10^{-1} / 1 \times 10^{-2}$	-3.3	-3.9	-10.8
$5 \times 10^{-2} / 5 \times 10^{-3}$	22.4	10.7	5.4
$1 \times 10^{-2} / 1 \times 10^{-3}$	31.0	24.9	20.3
$5 \times 10^{-3} / 5 \times 10^{-4}$	37.0	26.4	25.2
$1 \times 10^{-3} / 1 \times 10^{-4}$	37.2	26.5	26.0
$5 \times 10^{-4} / 5 \times 10^{-5}$	37.5	27.6	27.2
$1 \times 10^{-4} / 1 \times 10^{-5}$	37.5	27.7	27.2

Table 2

The values of the observed membrane potential E_m [mV] across cobalt sulphide membrane at $25 \pm 0.1^\circ\text{C}$

Electrolyte Concentration/Mol L ⁻¹ C_{II}/C_I	KCl	NaCl	LiCl
$1 \times 10^{-1} / 1 \times 10^{-2}$	7.6	-2.7	-11.5
$5 \times 10^{-2} / 5 \times 10^{-3}$	24.8	18.9	0.1
$1 \times 10^{-2} / 1 \times 10^{-3}$	36.2	24.2	18.9
$5 \times 10^{-3} / 5 \times 10^{-4}$	36.8	24.7	22.5
$1 \times 10^{-3} / 1 \times 10^{-4}$	37.0	26.2	23.0
$5 \times 10^{-4} / 5 \times 10^{-5}$	38.5	26.5	24.0
$1 \times 10^{-4} / 1 \times 10^{-5}$	38.5	26.5	24.1

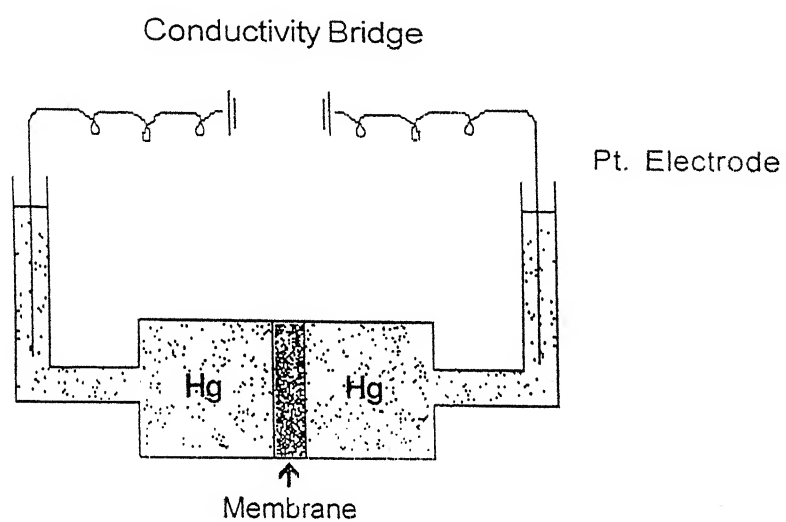


FIG. - 1

Cell for measuring the electrical
conductivity of membrane

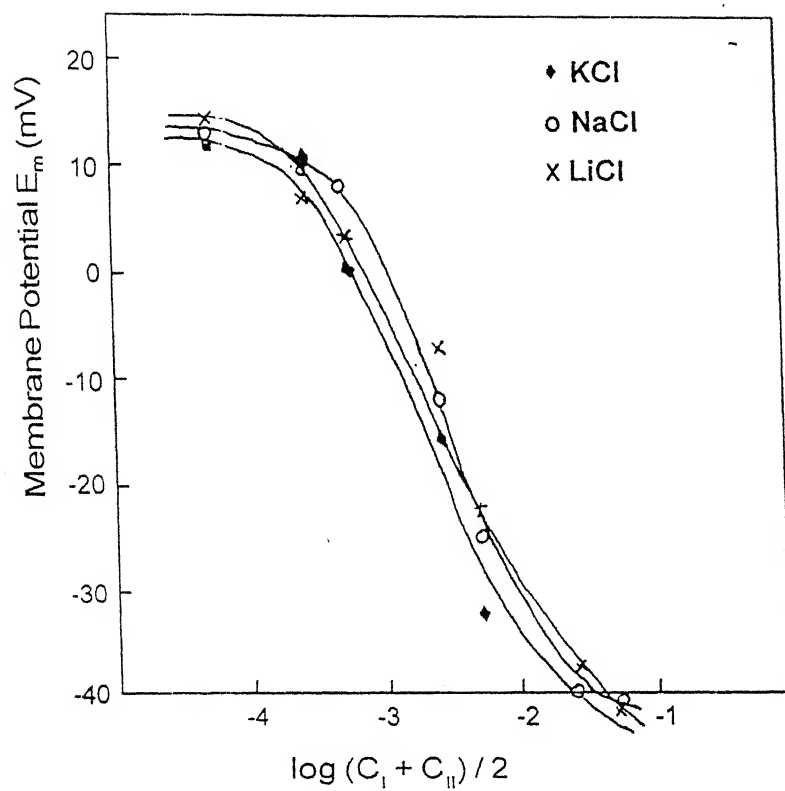


FIG. - 2

Plots of membrane potential E_m (mV) against $\log (C_I + C_{II}) / 2$ using 1:1 electrolytes across nickel sulphide membrane

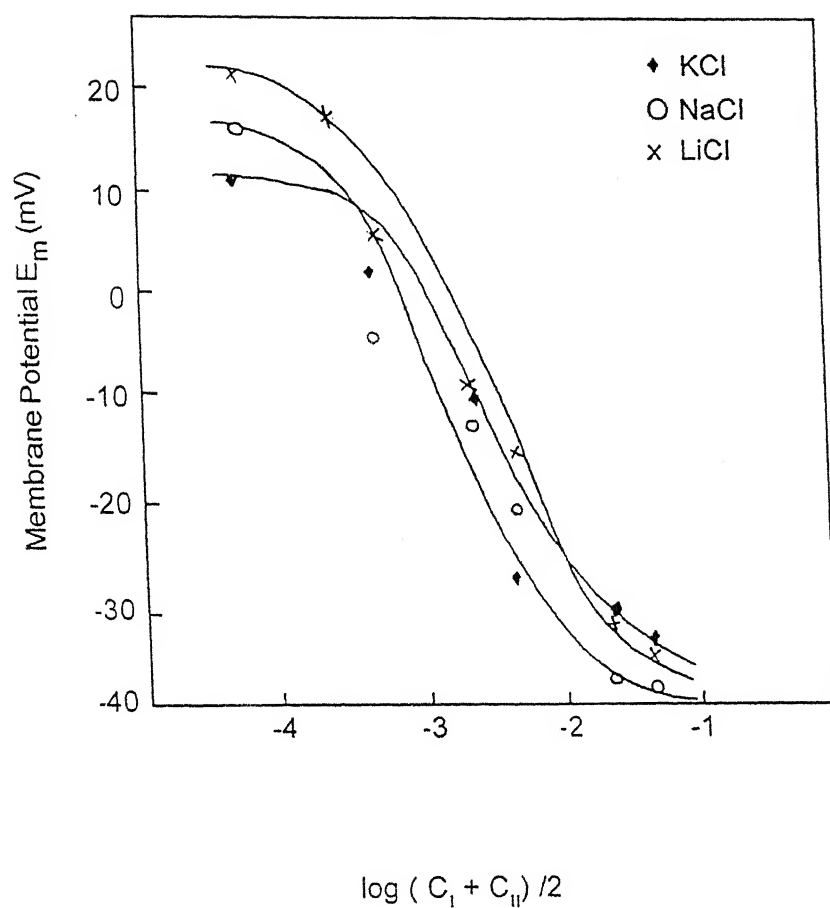


FIG. - 3

Plots of membrane potential E_m (mV) against $\log (C_I + C_{II}) / 2$ using 1:1 electrolytes across cobalt sulphide membrane

In the absence of pressure or temperature gradient, the generation of a steady e.m.f between two solutions of an electrolyte of different concentrations separated by a membrane, can be attributed to the presence of net charge on the membranes. Such charges play an important role in the sorption and transport of simple electrolytes in artificial as well as natural membranes [32-34] and impart some important electrochemical properties of coions, counter ions and neutral molecules. Hence, for detailed investigation of membrane selectivity, its thermodynamically effective fixed charge density is to be determined. It can be evaluated by making the use of an equation derived on the basis of thermodynamics of irreversible processes. This approach employs a phenomenological coefficient to correlate the gradients that exist across a membrane and their resulting fluxes.

Kobatake and coworkers [35,36] integrated basic flow equations, provided by thermodynamics of irreversible processes to derive the following equation for the degree of permselectivity $[P_s]$ of the membrane electrolyte system by taking into consideration an ionizable membrane in contact with solutions of monovalent electrolyte of concentrations C_I and C_{II} [$C_{II} > C_I$].

$$P_s \frac{1 - t_{app} - \alpha}{\alpha - (2\alpha - 1)(1 - t_{app})} = \frac{1}{(4\xi^2 + 1)^{1/2}} \quad [1]$$

where α , ξ and t_{app} are membrane parameter, i.e., fraction of ionic mobility ratio, relative concentration and the apparent transference number of co ions in membrane phase. Further, these can be expressed as:

$$\alpha = U_+^0 / [U_+^0 + U_-^0] \quad [2]$$

where U^0 is mobility of ionic species.

$$\xi = C / \phi X \quad [3]$$

$$E_m = - [RT / F] [1 - 2 t_{app}] \ln C_{||} / C_l \quad [4]$$

When the average external salt concentration, $C = [C_l + C_{||}] / 2$, is high in comparison with the thermodynamically effective fixed charge density ϕX , i.e., $\xi \gg 1$, the membrane potential can be expressed as

$$E_m = - [RT / F] [2\alpha - 1] \ln C_{||} / C_l \quad [5]$$

On the other hand, when the salt concentration is very low, the membrane potential expression becomes

$$E_m = - [RT / F] \ln C_{||} C_l \quad [6]$$

If the membrane potential follows the eqn. [6], the membrane may be referred as a perfectly permselective, where t_{app} becomes zero and P_s tends to unity. On the other hand, when membrane potential follows eqn. [5], t_{app} becomes $[1 - \alpha]$ and P_s equal to zero. Hence, It can be said that P_s takes a value between zero and unity depending on the external salt concentration for a given system of a membrane and on an electrolyte pair.

In accordance with eqn. [1], the straight line plot of P_s values given in Tables 3 & 4 of membranes against $(4\xi^2 + 1)^{-1/2}$ are shown in Figs.-4 and 5, which confirms the applicability of the irreversible thermodynamic approach to our model system when the average concentration, C and the thermodynamically effective fixed charge density, ϕX , are of the same magnitude, ξ becomes equal to unity and P_s equal to $1/\sqrt{5}$. The magnitude of concentration corresponding to this value of P_s is a measure of ϕX .

Table 3

The values of permselectivity P_s of the membrane using various 1:1 electrolytes at different concentration for nickel sulphide membrane.

Electrolyte Concentration/Mol L ⁻¹ C_{II}/C_I	KCl	NaCl	LiCl
$1 \times 10^{-1}/1 \times 10^{-2}$	0.70	0.79	0.84
$5 \times 10^{-2}/5 \times 10^{-3}$	0.66	0.78	0.77
$1 \times 10^{-2}/1 \times 10^{-3}$	0.52	0.54	0.69
$5 \times 10^{-3}/5 \times 10^{-4}$	0.24	0.39	0.35
$1 \times 10^{-3}/1 \times 10^{-4}$	-0.12	0.05	0.19
$5 \times 10^{-4}/5 \times 10^{-5}$	-0.18	0.02	0.12
$1 \times 10^{-4}/1 \times 10^{-5}$	-0.22	-0.13	0.00

Table 4

The values of permselectivity P_s of the membrane using various 1:1 electrolytes at different concentration for cobalt sulphide membrane.

Electrolyte Concentration/Mol L ⁻¹ C_{II}/C_I	KCl	NaCl	LiCl
$1 \times 10^{-1}/1 \times 10^{-2}$	0.56	0.75	0.77
$5 \times 10^{-2}/5 \times 10^{-3}$	0.50	0.71	0.70
$1 \times 10^{-2}/1 \times 10^{-3}$	0.48	0.63	0.49
$5 \times 10^{-3}/5 \times 10^{-4}$	0.20	0.42	0.43
$1 \times 10^{-3}/1 \times 10^{-4}$	-0.20	0.30	0.19
$5 \times 10^{-4}/5 \times 10^{-5}$	-0.16	-0.02	0.00
$1 \times 10^{-4}/1 \times 10^{-5}$	-0.18	-0.07	-0.10

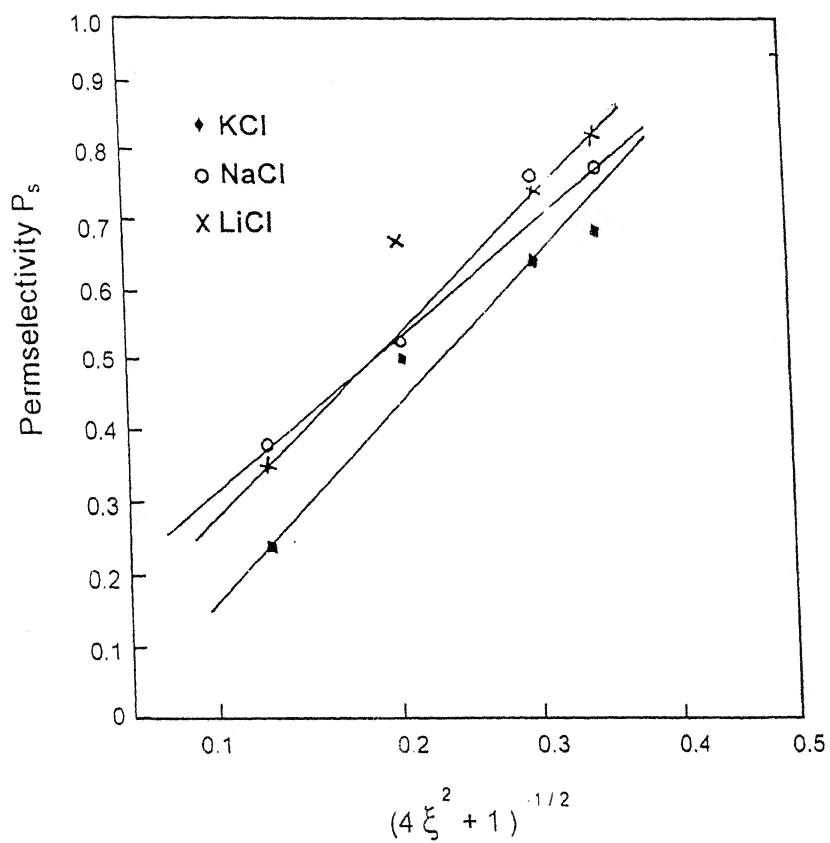


FIG. - 4

Plots of permselectivity P_s vs $\log (4\xi^2 + 1)^{-1/2}$ for nickel sulphide membrane.

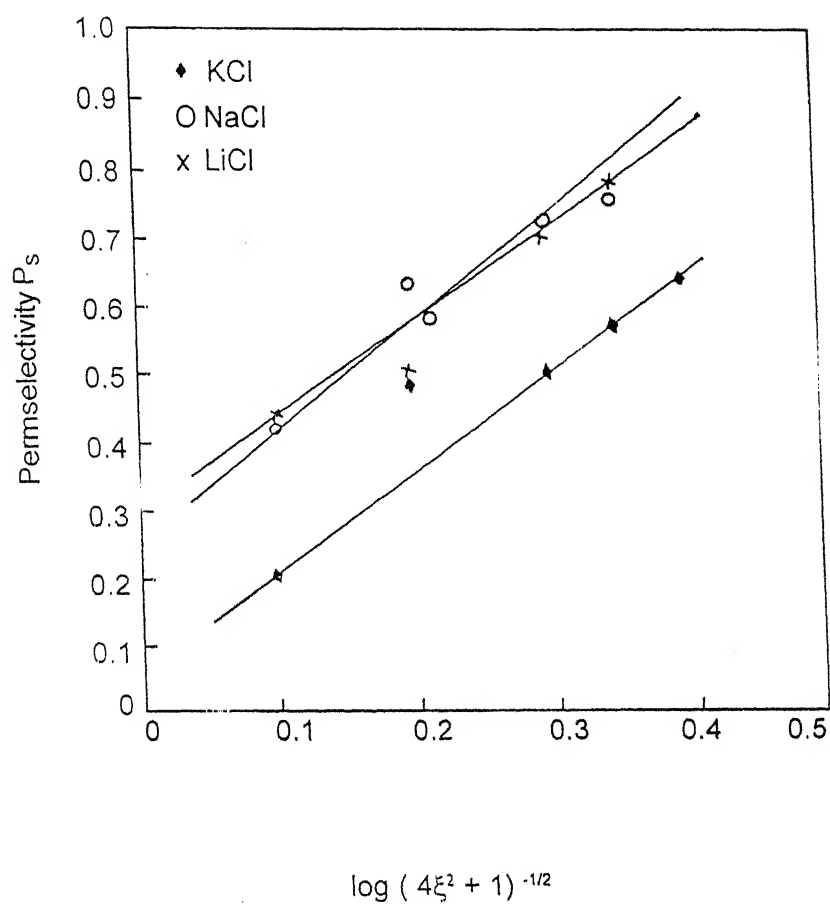


FIG. - 5

Plots of permselectivity P_s vs $\log (4 \xi^2 + 1)^{-1/2}$ for cobalt sulphide membrane.

Another theory developed by Tasaka and coworkers [37] has also been used in the evaluation of magnitude of ϕX . In the absence of an externally applied electric field or a pressure gradient at the limit of low electrolyte concentration [where the effect of flow of water is negligible], the expression for membrane potential can be written:

$$-E_m = \frac{RT}{f} \ln C_{II} / C_I \quad [7]$$

whereas at the limit of high electrolyte concentration we have:

$$-E_m = \frac{RT}{F} \left(\frac{r-1}{r} \right) \left(\frac{\phi x}{2} \right) 1/C_I$$

[8]

which predicts a linear relationship between E_m and $1/C_I$ and allows the evaluation of ϕX from the slope of straight lines obtained by plotting E_m against $1/C_I$.

The effective fixed charge density, ϕX , has also been related to E_m and t_- as [38]

$$(F/RT)E_m = -\ln \gamma + \ln \frac{-\phi X + \sqrt{(\phi X)^2 + 4X_{II}^2}}{-\phi X + \sqrt{(\phi X)^2 + 4C_I^2}} + (2t_- - 1) \ln \left[\frac{(1-2t_-)\phi X + \sqrt{(\phi X)^2 + 4C_{II}^2}}{(1-2t_-)\phi X + \sqrt{(\phi X)^2 + 4C_I^2}} \right] \quad [9]$$

which can be approximated to eqn. [10] if the membrane is slightly charged.

$$(F/RT)E_m = (2t_- - 1) \ln \gamma + \frac{2(\gamma - 1)}{\gamma} t_- (1 - t_-) \frac{\phi X}{C_I} \quad [10]$$

This equation predicts a straight line plot of $(F/RT) E_m$ versus $1/C_I$ at fixed γ , and allows the evaluation of t_- and ϕX from the intercept and slope of the linear plot.

Equations [1], [8] and [10] have been utilized to calculate the effective fixed charge density values tables 5 and 6, and the values of transference number t which are given in Tables 7 and 8. The values of transference number t are plotted against $\log 1/C_I$ as shown in Figs. 6 and 7. The plots of P_s versus $\log [C_I + C_{II}]/2$ are shown in Figs. 8 and 9, E_m versus $1/C_I$ are shown in Figs. 10 and 11, and $(F/RT) E_m$ versus $1/C_I$ are shown in Figs. 12 and 13. As the values of ϕX are quite low, the membranes used in this investigation were expected to have a low negative electrostatic field strength of the fixed charge sites. For such a situation following the Eisenman and Horn [30], selectivity sequence of metal ions was proposed as:



The same sequence has also already been studied by Eisenman and Horn [30] which also strengthens to our work.

The selectivity sequence of nickel and cobalt sulphide membranes for the metal ions of the same sign, is also confirmed by various experimental methods as :

BI-IONIC METHOD :

The steady e.m.f. of a biionic cell, containing two electrolytes of the type iX and jX [or iX and iY] separated by a membrane, is called the biionic potential [BIP] [39], which is the measure of the selectivity of the membrane for ions of the same sign. The BIP has also been considered by Hellferich [15], in accordance with the concepts of the TMS theory [9,10], as being the algebraic sum of the two interfacial potentials and an internal diffusion potential. A complete mathematical discussion under the conditions: [a]

Table 5

The values of effective fixed charge density ϕX of nickel sulphide membrane using various 1:1 electrolytes derived from different theories.

Electrolyte	KCl	NaCl	LiCl
Kobatake & Coworkers [35, 36]	2.2×10^{-3}	2.2×10^{-3}	2.2×10^{-3}
Tasaka et al. [37]	0.1×10^{-3}	1.0×10^{-3}	1.2×10^{-3}
Aizawa et. al. [38]	1.2×10^{-3}	1.75×10^{-3}	2.05×10^{-3}

Table 6

The values of effective fixed charge density ϕX of cobalt sulphide membrane using various 1:1 electrolytes derived from different theories.

Electrolyte	KCl	NaCl	LiCl
Kobatake & Coworkers [35, 36]	3.5×10^{-3}	2.2×10^{-3}	2.2×10^{-3}
Tasaka et al. [37]	0.1×10^{-3}	0.07×10^{-3}	1.0×10^{-3}
Aizawa et. al. [38]	1.7×10^{-3}	1.3×10^{-3}	1.8×10^{-3}

Table 7

Transference number t_- of coions derived from observed membrane potential values at various electrolyte concentration through nickel sulphide membrane.

Electrolyte Concentration/Mol L ⁻¹ C_{II}/C_I	KCl	NaCl	LiCl
$1 \times 10^{-1}/1 \times 10^{-2}$	0.85	0.85	0.84
$5 \times 10^{-2}/5 \times 10^{-3}$	0.83	0.84	0.82
$1 \times 10^{-2}/1 \times 10^{-3}$	0.76	0.70	0.76
$5 \times 10^{-3}/5 \times 10^{-4}$	0.62	0.60	0.55
$1 \times 10^{-3}/1 \times 10^{-4}$	0.46	0.42	0.46
$5 \times 10^{-4}/5 \times 10^{-5}$	0.41	0.41	0.43
$1 \times 10^{-4}/1 \times 10^{-5}$	0.34	0.34	0.37

Table 8

Transference number t_- of coions from derived from observed membrane potential at various electrolyte concentration through cobalt sulphide membrane.

Electrolyte Concentration/Mol L ⁻¹ C_{II}/C_I	KCl	NaCl	LiCl
$1 \times 10^{-1}/1 \times 10^{-2}$	0.78	0.82	0.81
$5 \times 10^{-2}/5 \times 10^{-3}$	0.75	0.80	0.77
$1 \times 10^{-2}/1 \times 10^{-3}$	0.74	0.68	0.63
$5 \times 10^{-3}/5 \times 10^{-4}$	0.60	0.62	0.58
$1 \times 10^{-3}/1 \times 10^{-4}$	0.69	0.54	0.45
$5 \times 10^{-4}/5 \times 10^{-5}$	0.42	0.41	0.37
$1 \times 10^{-4}/1 \times 10^{-5}$	0.47	0.37	0.33

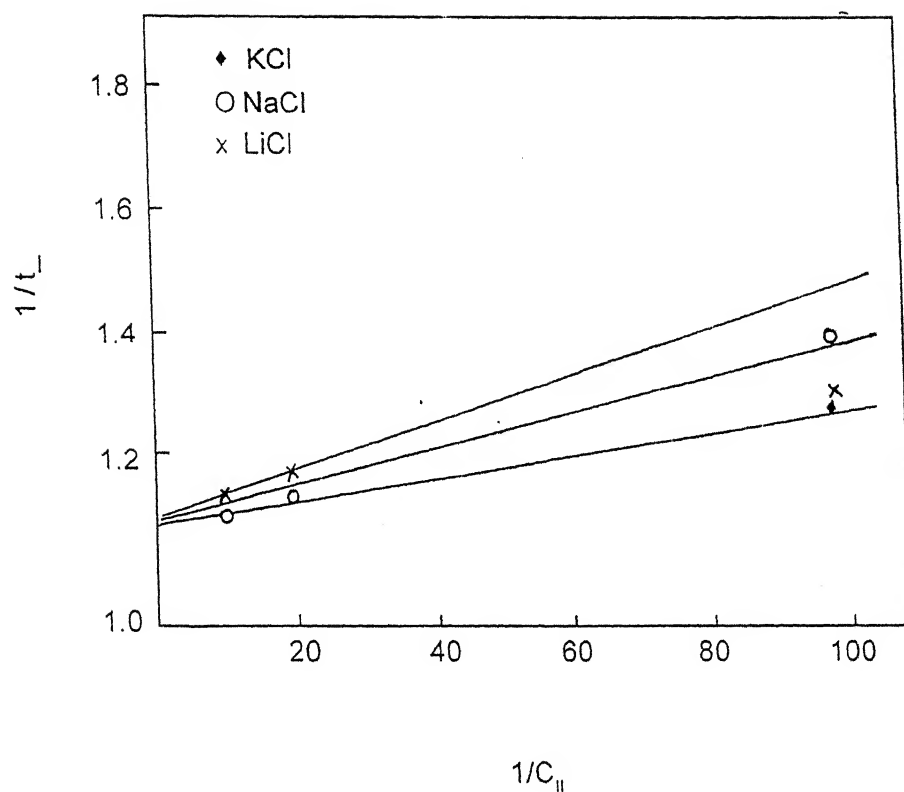


FIG. - 6

Plots of transference number (t_-) against $1/C_{II}$ of various 1:1 electrolytes at different concentration across nickel sulphide membrane.

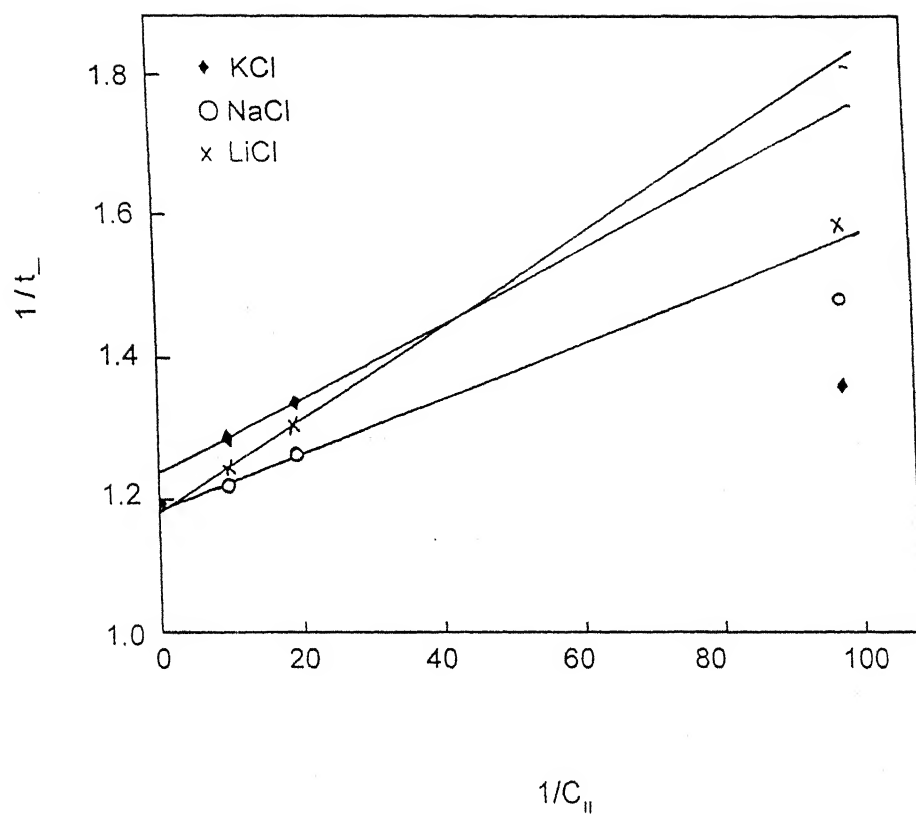


FIG. - 7

Plots of transference number (t_-) against $1/C_{II}$ of various 1:1 electrolytes at different concentration across cobalt sulphide membrane.

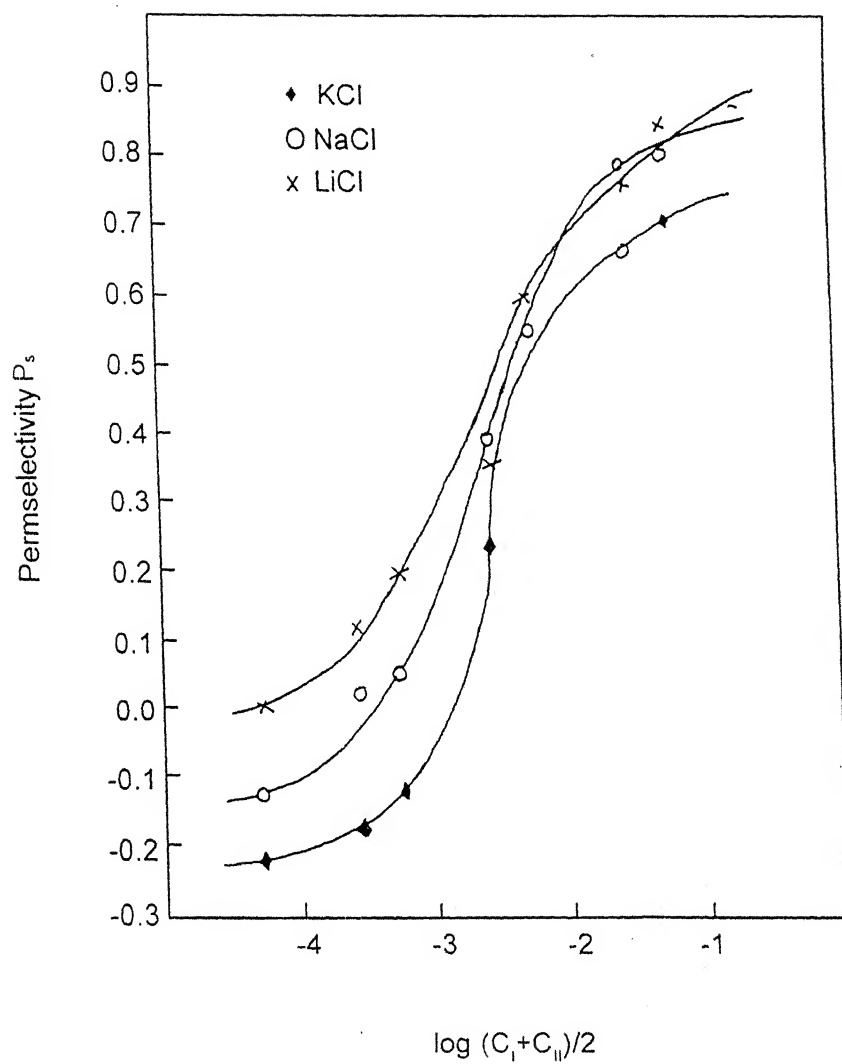


FIG. - 8

Plots of permselectivity P_s vs $\log (C_I + C_{II})/2$
for nickel sulphide membrane.

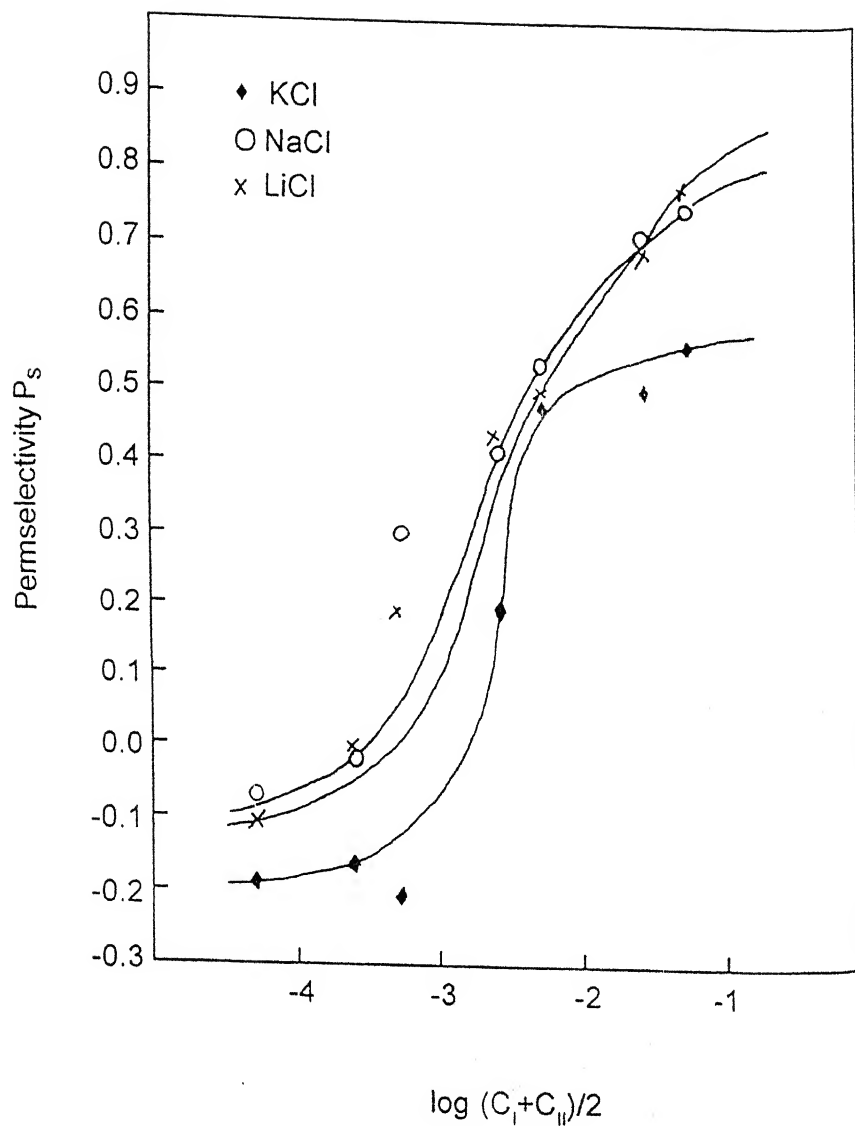


FIG. - 9

Plots of permselectivity P_s vs $\log (C_I + C_{II})/2$
for cobalt sulphide membrane.

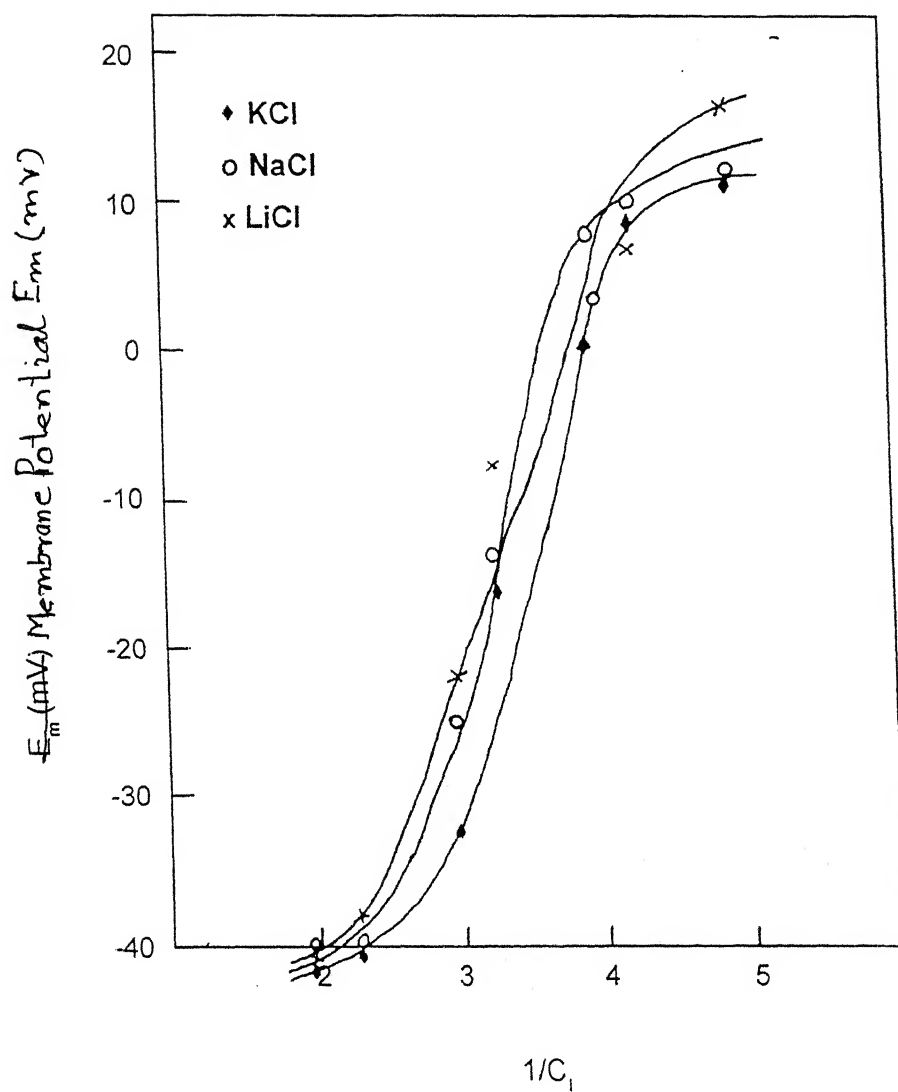


FIG. - 10

Plots of Membrane Potential E_m (mV) vs. $1/C_1$
for nickel sulphide membrane

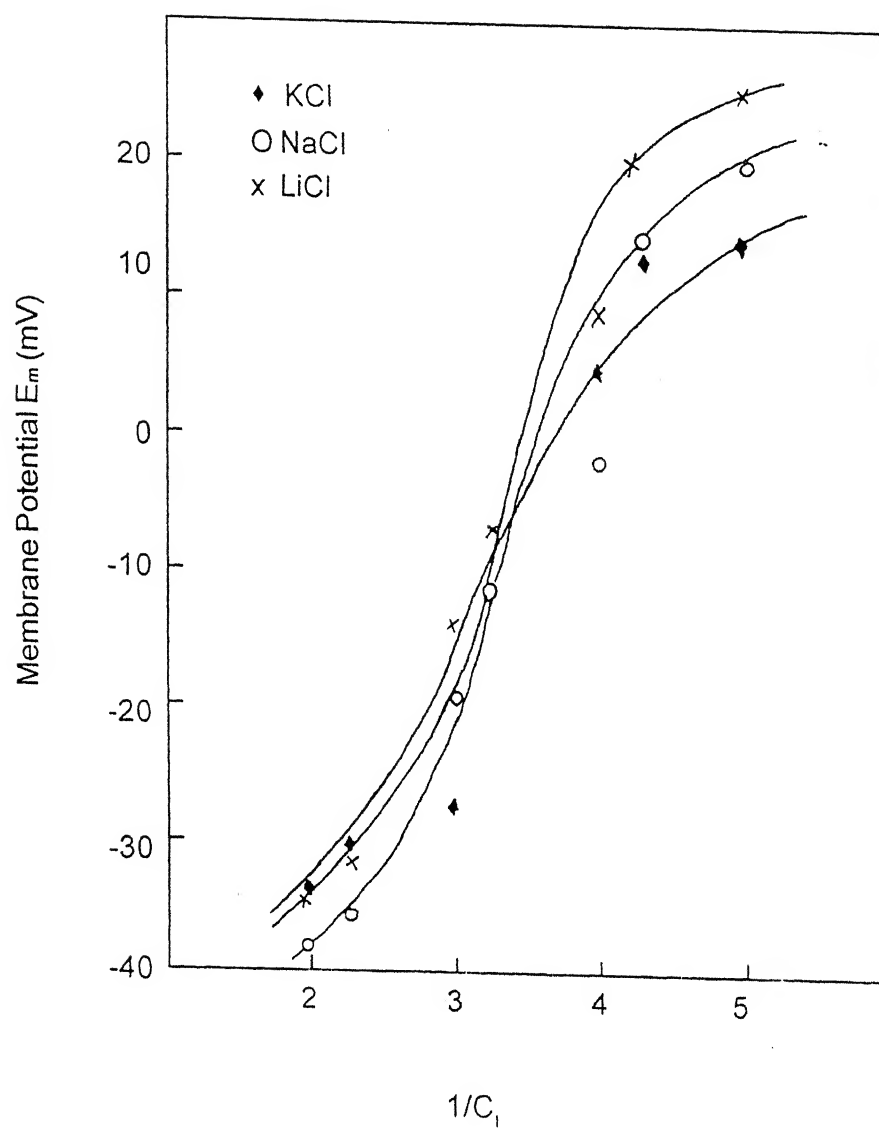


FIG. - 11

Plots of Membrane Potential E_m (mV) vs. $1/C_1$
for cobalt sulphide membrane

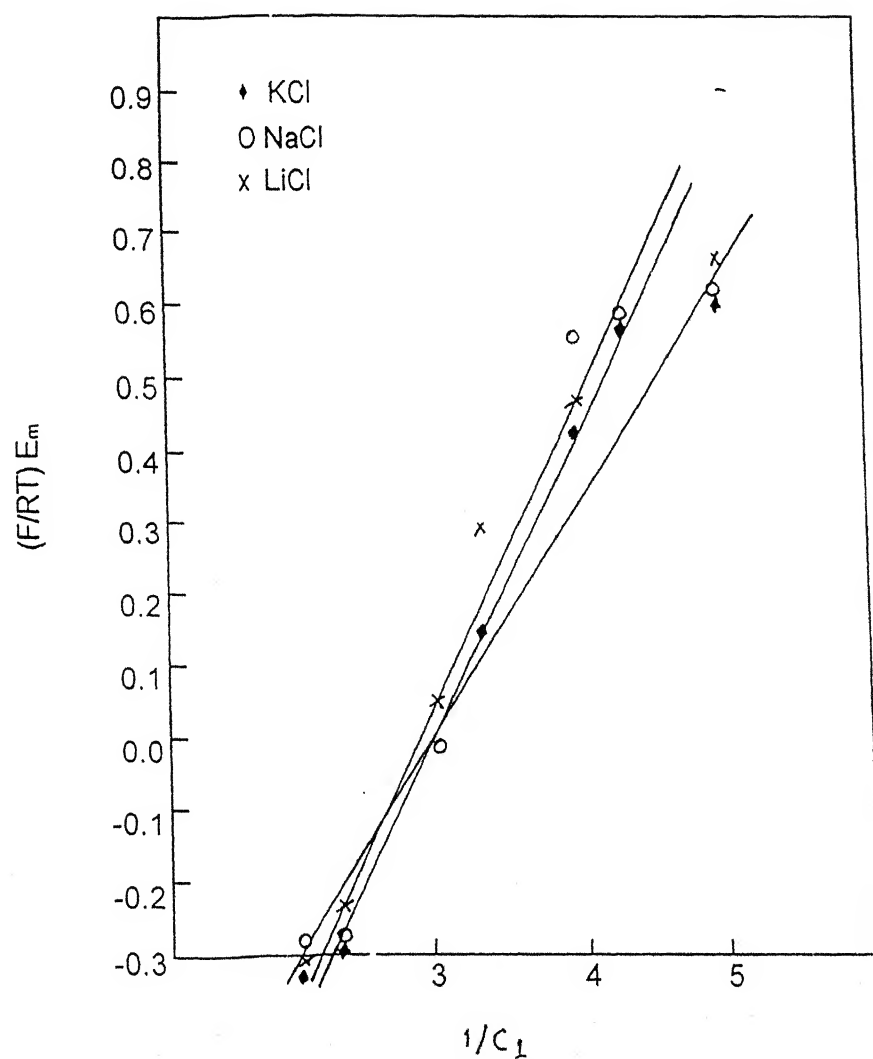


FIG. - 12

Plots of $(F/RT) E_m$ (mV) vs. $1/C_1$
for nickel sulphide membrane

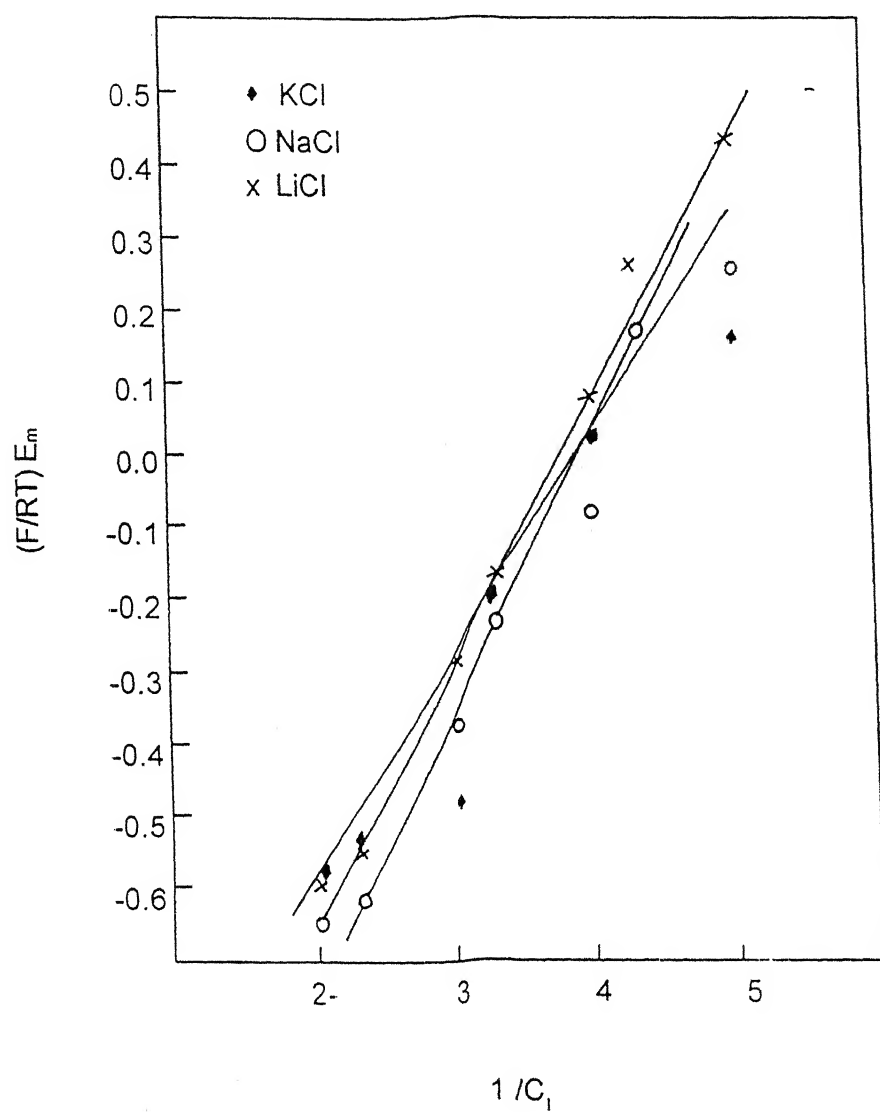


FIG. - 13

Plots of $(F/RT) E_m$ (mV) vs. $1/C_1$
for cobalt sulphide membrane

membrane diffusion control, [b] film diffusion control, and [c] coupled membrane film diffusion control has been presented [15]. For a general case involving complete membrane diffusion control, the total BIP for counter ions is given by

$$E = \frac{RT}{zF} \ln \frac{\bar{D}_i a'_j K_i}{\bar{D}_j a''_j \bar{V}_i K_j} = \ln \left[K_{ji} \left(\frac{\bar{D}_i a'_i v_j}{\bar{D}_j a''_j v_i} \right) \right] \quad [11]$$

where $a'_i/a''_j, \bar{D}_i/\bar{D}_j, \bar{V}_i/\bar{V}_j$ are the ratio of the activities, diffusion coefficients and the activity coefficients of the counter ions i and j respectively. Overbars refer the phenomena in the membrane phase, R , T , z and F have their usual meanings. Using the Einstein relation $D_i = U_i RT$ and the generalized Nernst equation in which the permeability ratio are independent of the external electrolyte solution [14, 40] the eqn. [11] reduces to the form

$$E = \frac{RT}{zF} \ln \left[\frac{a'_i \bar{U}_i}{a''_j \bar{U}_j} K_{ji} \right] = \frac{RT}{zF} \ln \left[\frac{a'_i \bar{P}_i}{a''_j \bar{P}_j} \right] \quad [12]$$

this eqn. [12] gives $\bar{P}_i/\bar{P}_j = K_{ji} \bar{U}_i/\bar{U}_j$

This equation has also been derived by Sandblom and Eisenman [17] from thermodynamic treatment for fixed site membranes which implies that the permeability ratio is quite generally related to the ion equation [12] gives exchange equilibrium constant K_{ji} and the ratio of mobilities of the critical ions. Further, using the well known relation

$$\bar{U}_i/\bar{U}_j = \bar{\lambda}_i/\bar{\lambda}_j \quad [13]$$

eq. [13] gives

$$\bar{P}_i/\bar{P}_j = K_{ji} \bar{U}_i/\bar{U}_j = K_{ji} \bar{\lambda}_i/\bar{\lambda}_j \quad [14]$$

where $\bar{\lambda}_i$ is the conductivity of the membrane when it is wholly in i form and $\bar{\lambda}_j$ is the conductivity of the membrane when it is wholly in the j form.

The quantity \bar{P}_i/\bar{P}_j is considered truly a membrane property [17]. It is independent of the changes made in the activities a_i and a_j of the external solution. Thus it is apparent from eqn. [12] that a plot of $\log a_i$ against potential for a constant a_j should give a straight line. Similarly a straight line should be obtained if a_j is varied and a_i is kept constant. Both these lines should show potential changes of RT/F or 59.2 mV at 25° C for each tenfold changes in activity when membranes are separating 1:1 electrolytes. Accordingly, BIP values across parchment supported nickel and cobalt sulphide membranes were determined for various electrolyte pairs, viz. KCl-NaCl, KCl-LiCl and NaCl-LiCl, taking the concentration of one of the electrolyte constant [0.01 M] and varying the concentration of the other electrolyte between 0.001 M to 0.01 M. In second set of experiment the concentration of other electrolyte was kept constant and the concentration of the first electrolyte was varied in same range. The biionic potentials thus observed were plotted against logarithm of the mean molal activity. Two sets of straight lines in accordance with the expectation of eqn. [12] are obtained as shown in Figs. 14 and 15. The straight lines confirm the views of Beg and Eisenman [14, 40] that the permeability values are independent of external solution conditions. In order to derive the values of the permeability ratio, these straight lines were extended to cut the activity axis at zero potential. Thus two sets of a_i and a_j values for which potential E was zero, were obtained. At zero potential the ratio a_i / a_j was equal to \bar{P}_i/\bar{P}_j . The values of

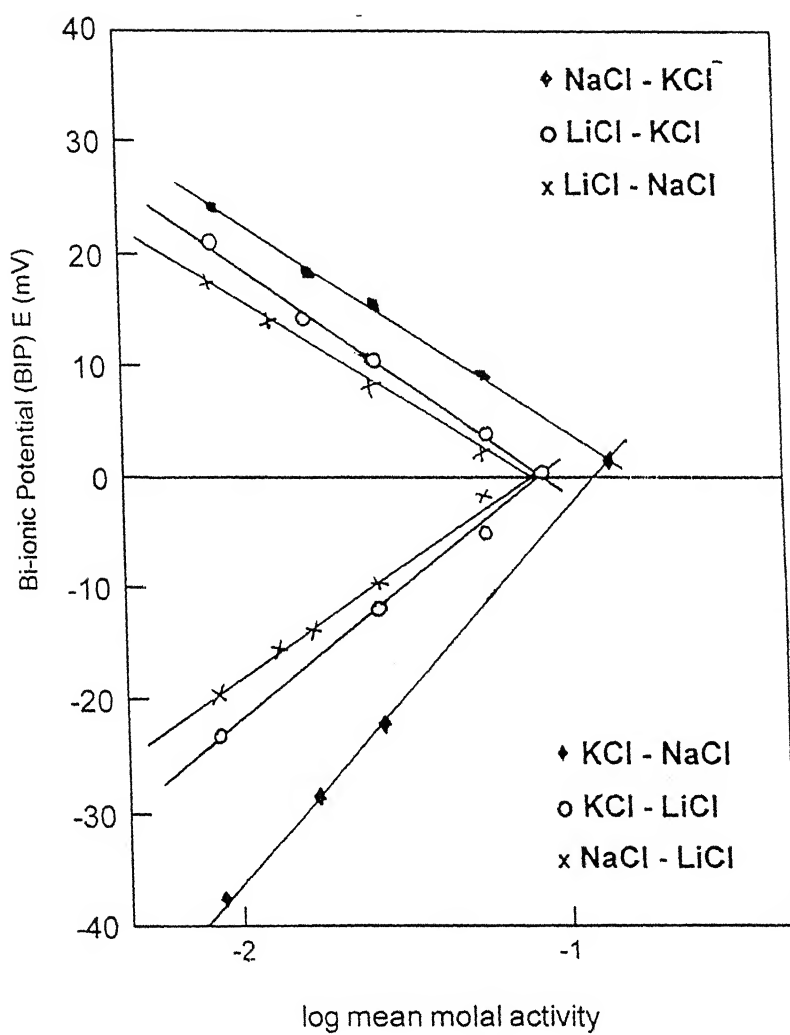


FIG. - 14

Plots of Biionic potential (BIP) E (mV) vs. logarithm of mean molal activity for nickel sulphide membrane.

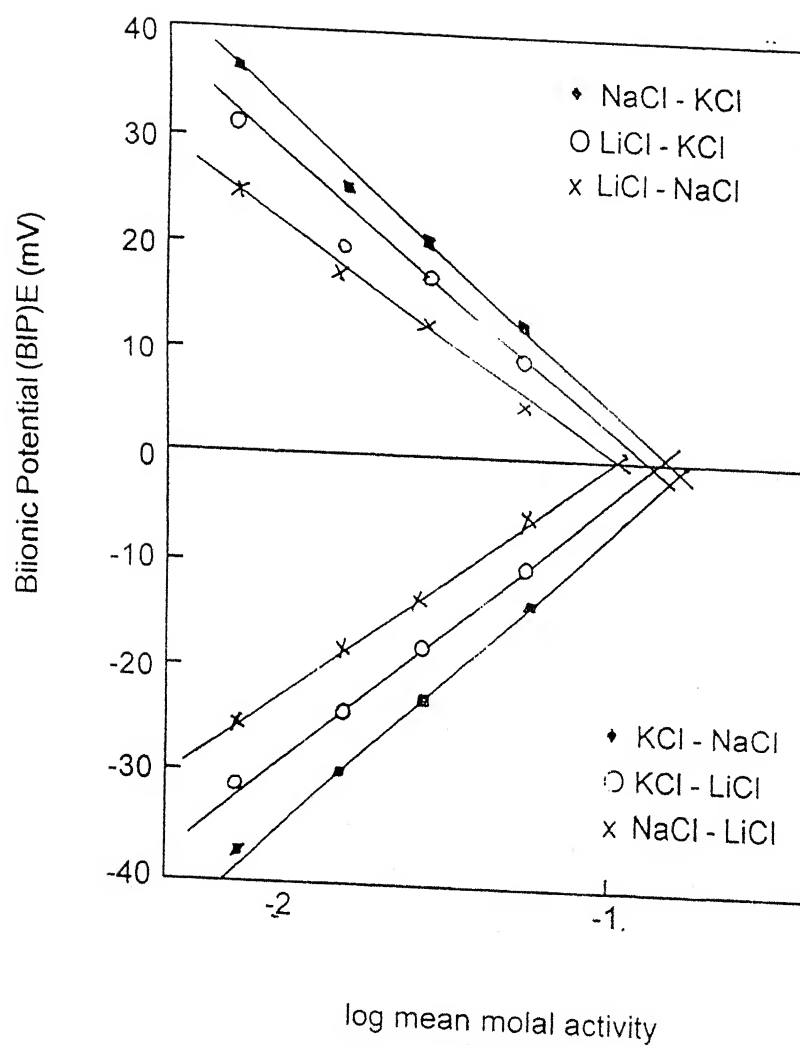


FIG. - 15

Plots of Biionic potential (BIP) E (mV) vs. logarithm of mean molal activity for cobalt sulphide membrane.

\bar{P}_i/\bar{P}_j derived in this way for the nickel and cobalt sulphide membranes for different electrolyte pairs are as follows :

for nickel sulphide membrane

$$\bar{P}_{K^+}/\bar{P}_{Na^+} = 1.72, \bar{P}_{K^+}/\bar{P}_{Li^+} = 1.50, \bar{P}_{Na^+} = 1.36$$

for cobalt sulphide membrane.

$$\bar{P}_{K^+}/\bar{P}_{Na^+} = 1.99, \bar{P}_{K^+}/\bar{P}_{Li^+} = 1.71, \bar{P}_{Na^+} = 1.18$$

The values of \bar{P}_i/\bar{P}_j are generally low which point towards the fact that the membranes are relatively more imbibed in an equilibrium water content [41]. The values of the intramembrane permeability ratio also refer to the selectivity sequence of the membranes for the cations of the following order:

$$K^+ > Na^+ > Li^+$$

This order of selectivity on the basis of the Eisenman-Sherry model of membrane selectivity [40,42-43] points towards the weak field strength of the charge groups attached to the membrane matrix. This is in accordance with our earlier findings of charge density [charge density $\simeq 10^{-3}$ mol l^{-1}] determinations of nickel and cobalt sulphide membranes [4].

Biionic potential measurements were also carried out by interposing the membrane between two different electrolyte solutions at the same concentration. The BIP values were low when the membrane was used to separate concentrated electrolyte solutions whereas, it increased with decreasing salt concentrations. In this way experimentally observed values of BIP across both membranes are given in Tables 9 and 10 and this change is depicted in Figs. 16 and 17. The permeability ratio \bar{P}_i/\bar{P}_j calculated from

Table 9

Experimental values of biionic potential [BIP] E [mV] across nickel sulphide membrane at $25 \pm 0.1^\circ\text{C}$

Electrolyte Concentration / Mol L ⁻¹	KCl-NaCl	KCl-LiCl	NaCl - LiCl
$1 \times 10^{-1} / 1 \times 10^{-1}$	2.26	-3.94	-2.26
$5 \times 10^{-2} / 5 \times 10^{-2}$	4.54	-2.74	-2.03
$1 \times 10^{-2} / 1 \times 10^{-2}$	8.57	2.60	2.24
$5 \times 10^{-3} / 5 \times 10^{-3}$	11.65	3.45	4.15
$1 \times 10^{-3} / 1 \times 10^{-3}$	19.84	16.00	13.46

Table 10

Experimental values of biionic potential [BIP] E [mV] across cobalt sulphide membrane at $25 \pm 0.1^\circ\text{C}$

Electrolyte Concentration / Mol L ⁻¹	KCl-NaCl	KCl-LiCl	NaCl - LiCl
$1 \times 10^{-1} / 1 \times 10^{-1}$	2.41	-4.52	-4.21
$5 \times 10^{-2} / 5 \times 10^{-2}$	2.55	-2.46	-2.46
$1 \times 10^{-2} / 1 \times 10^{-2}$	6.80	2.62	0.99
$5 \times 10^{-3} / 5 \times 10^{-3}$	13.30	5.11	3.45
$1 \times 10^{-3} / 1 \times 10^{-3}$	14.80	18.50	9.76

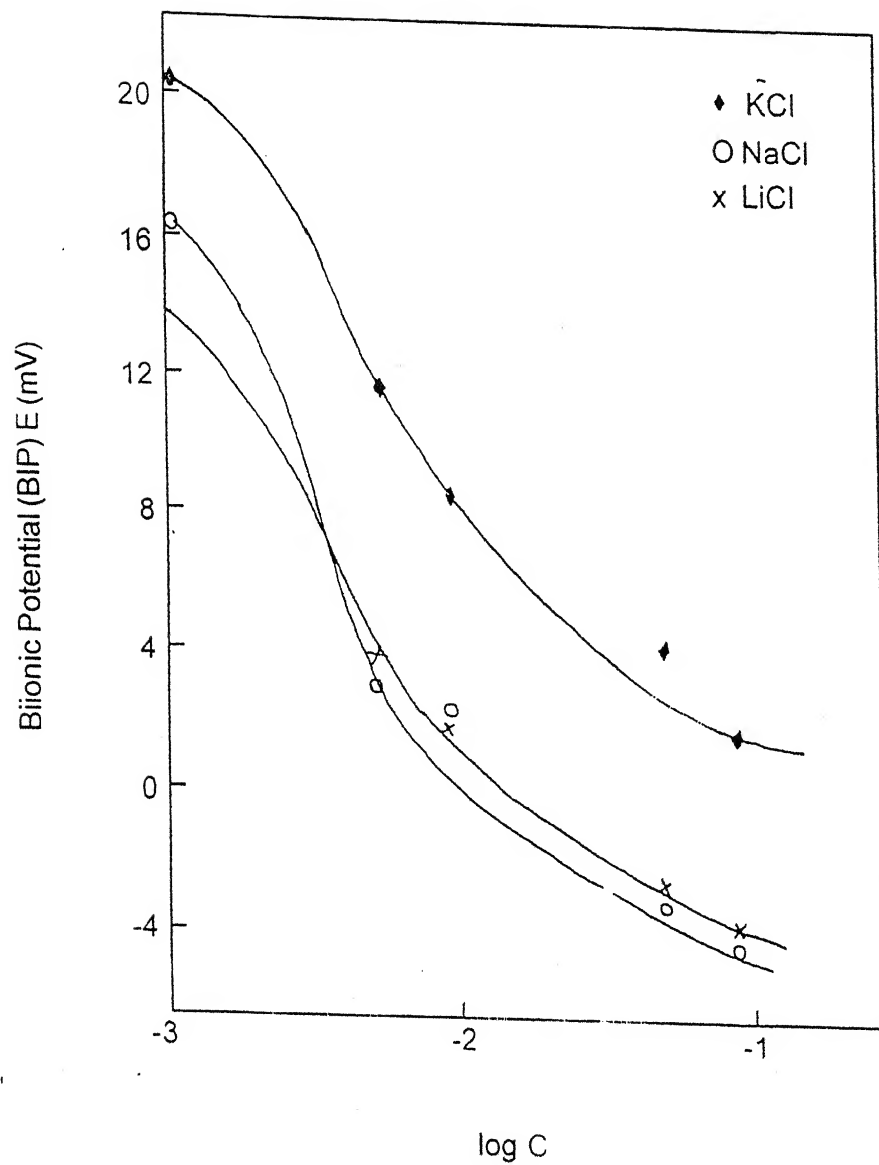


FIG. - 16

Plots of Biionic potential (BIP) E (mV) vs. logarithm C
for nickel sulphide membrane

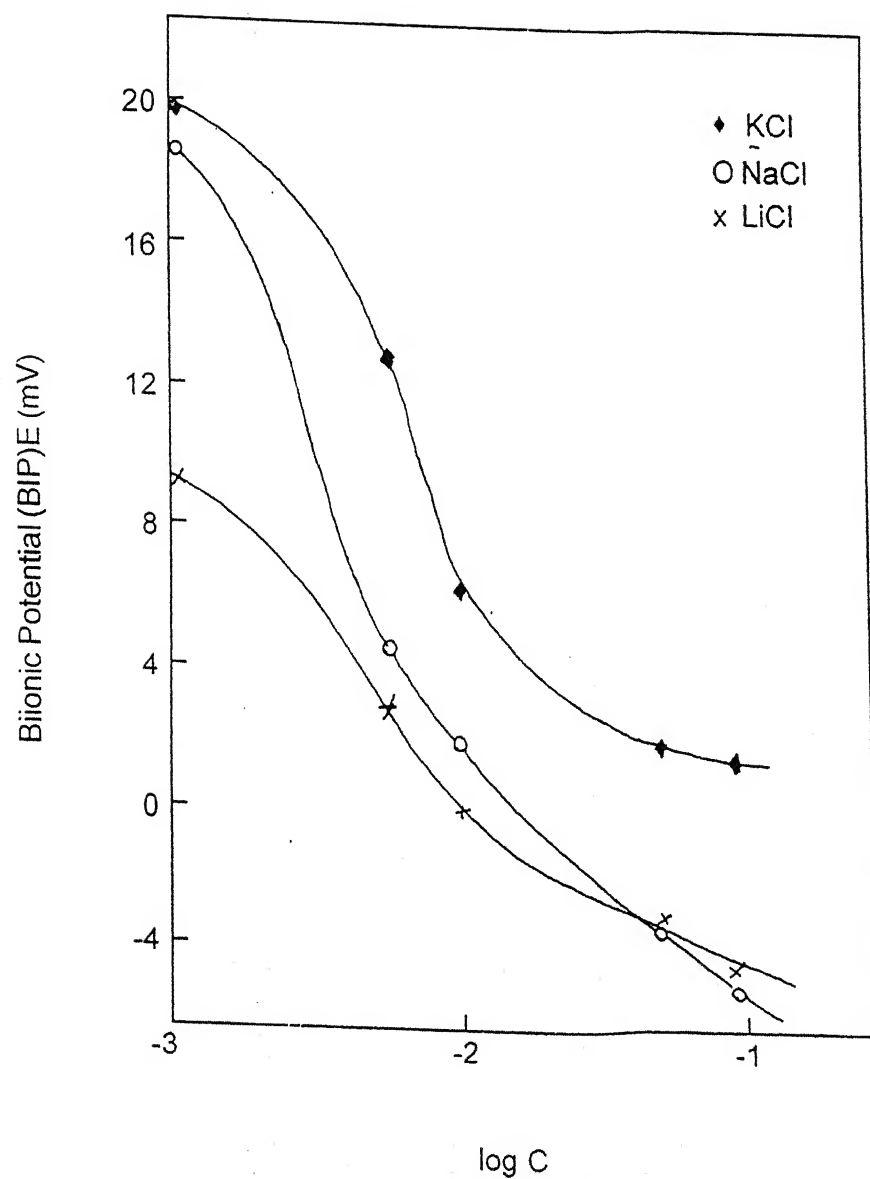


FIG. - 17

Plots of Biionic potential (BIP) E (mV) vs. logarithm C
for cobalt sulphide membrane

BIP values using eqn. [12] given in Tables 11 and 12, were also seen concentration dependent. The variation in BIP caused by the changes produced in the permeability ratio may be ascribed due to structural changes produced at the membrane solution interfaces. Parchment supported inorganic precipitated membranes contain exchangeable groups as part of its structure which may account for its negative charge. The exchangeable cations will be free to move in the pores. Within the pores there will be a diffuse ionic atmosphere from the charged wall. Since the membrane under investigation carries low ionic charge densities [i. e., charge density of the order $1 \times 10^{-3} \text{ mol l}^{-1}$], anion encroachment into membrane seems to be the most probable phenomenon. The thickness of the atmosphere depends upon the electrolyte concentration. In very dilute solutions of electrolyte, the thickness of anions becomes so great that only cations are present in the pores and the membranes become impermeable to anions, which is actually a condition necessary for the derivation of eqn. [12] with constant permeability ratio. Thus the best data on \bar{P}_i/\bar{P}_j are that from the most dilute solutions. It may, therefore, be concluded that the existence of an expression for E with constant permeability ratios can not be characteristic of all the membranes but it is restricted to certain physical situations, most notably, those in which a membrane is permeable only to species of one sign. This is an agreement with the mathematical treatment advanced by Sandblom and Eisenman [17].

In order to have a knowledge of selectivity K_{ij} from the predetermined values of \bar{P}_i/\bar{P}_j the ratio of electrical conductivities $\bar{\lambda}_i/\bar{\lambda}_j$ as demanded by

Table 11

Values of the intramembrane permeability ratios (\bar{P}_i/\bar{P}_j) of various 1:1 electrolyte ion pairs for nickel sulphide membrane.

Electrolyte ion pair Concentration / Mol L ⁻¹	KCl-NaCl	KCl-LiCl	NaCl - LiCl
1x10 ⁻¹ /1x10 ⁻¹	1.09	0.80	0.88
5x10 ⁻² /5x10 ⁻²	1.19	0.90	0.92
1x10 ⁻² /1x10 ⁻²	1.44	1.09	1.09
5x10 ⁻³ /5x10 ⁻³	1.57	1.14	1.19
1x10 ⁻³ /1x10 ⁻³	2.17	1.86	1.68

Table 12

Values of the intramembrane permeability ratios (\bar{P}_i/\bar{P}_j) of various 1:1 electrolyte ion pairs for cobalt sulphide membrane.

Electrolyte ion pair Concentration / Mol L ⁻¹	KCl-NaCl $\frac{\bar{P}_{K^+}}{\bar{P}_{Na^+}}$	KCl-LiCl $\frac{\bar{P}_{K^+}}{\bar{P}_{Li^+}}$	NaCl - LiCl $\frac{\bar{P}_{Na^+}}{\bar{P}_{Li^+}}$
1x10 ⁻¹ /1x10 ⁻¹	1.10	0.83	0.84
5x10 ⁻² /5x10 ⁻²	1.24	0.90	0.90
1x10 ⁻² /1x10 ⁻²	1.30	1.10	1.04
5x10 ⁻³ /5x10 ⁻³	1.68	1.22	1.14
1x10 ⁻³ /1x10 ⁻³	2.16	1.45	1.46

eqn. [14] must be known. Membrane conductance measurements were carried out when it was wholly in the form i or wholly in the form j. The values of membrane conductance at various electrolyte concentration of both the membranes as given in Tables 13 and 14, which are relatively more dependent upon the concentration of the electrolyte within the membranes as shown in Figs. 18 and 19. This implies that the membranes have a relatively high Donnan uptake of anion and a low selectivity constant value. This is in agreement with the findings of Heyman and Rabinov [44], Spiegler et al. [45] and our own findings with ion exchange membranes [4-8]. The values of selectivity, K_{ij} evaluated from the ratio of electrical conductivities $\bar{\lambda}_i/\bar{\lambda}_j$, and the intramembrane permeability ratio \bar{P}_i/\bar{P}_j , using eqn. [14] are given in Tables 15 and 16.

MIXTURE METHOD :

To assess the selectivity sequence of the membranes for the cations, values of potentiometric selectivity constant K_{ij}^{Pot} have been evaluated using the methods developed by Dole [46], and modified and improved by Buck et al. [47, 48]. However, a number of methods [49] have been suggested for the determination of selectivity constant by taking the mixture of electrolytes across the membrane and measuring the electrical potentials developed. The general equation [eqn. 15] for membrane potential E in an electrochemical cell of the type

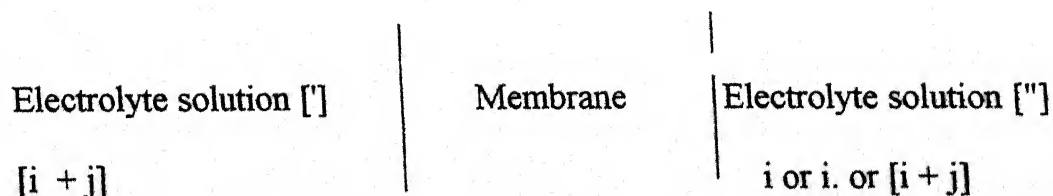


Table 13

Observed values of membrane conductance [Sm^{-1}] for monovalent electrolyte at $25 \pm 0.1^\circ\text{C}$ across nickel sulphide membrane.

Electrolyte Concentration / Mol L^{-1}	KCl-NaCl	KCl-LiCl	NaCl - LiCl
$1 \times 10^{-1} / 1 \times 10^{-1}$	0.91	0.52	0.35
$5 \times 10^{-2} / 5 \times 10^{-2}$	1.6	1.0	0.82
$1 \times 10^{-2} / 1 \times 10^{-2}$	3.4	2.6	2.2
$5 \times 10^{-3} / 5 \times 10^{-3}$	4.0	3.2	2.8
$1 \times 10^{-3} / 1 \times 10^{-3}$	8.0	7.0	6.8

Table 14

Observed values of membrane conductance [Sm^{-1}] for monovalent electrolyte at $25 \pm 0.1^\circ\text{C}$ across cobalt sulphide membrane.

Electrolyte Concentration / Mol L^{-1}	KCl-NaCl	KCl-LiCl	NaCl - LiCl
$1 \times 10^{-1} / 1 \times 10^{-1}$	0.64	0.62	0.41
$5 \times 10^{-2} / 5 \times 10^{-2}$	1.04	1.02	0.70
$1 \times 10^{-2} / 1 \times 10^{-2}$	3.6	3.5	2.4
$5 \times 10^{-3} / 5 \times 10^{-3}$	4.6	4.6	3.2
$1 \times 10^{-3} / 1 \times 10^{-3}$	8.0	7.8	5.0

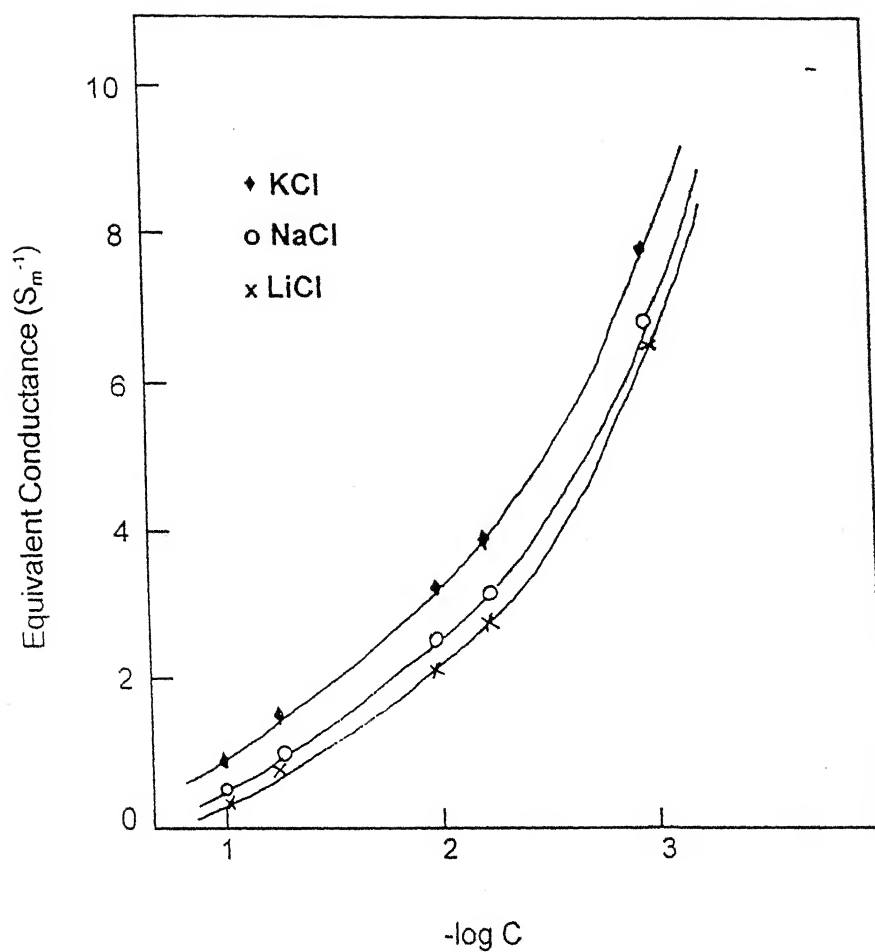


FIG. - 18

Typical plots of equivalent conductance (S_m^{-1}) vs. $-\log C$
for nickel sulphide membrane

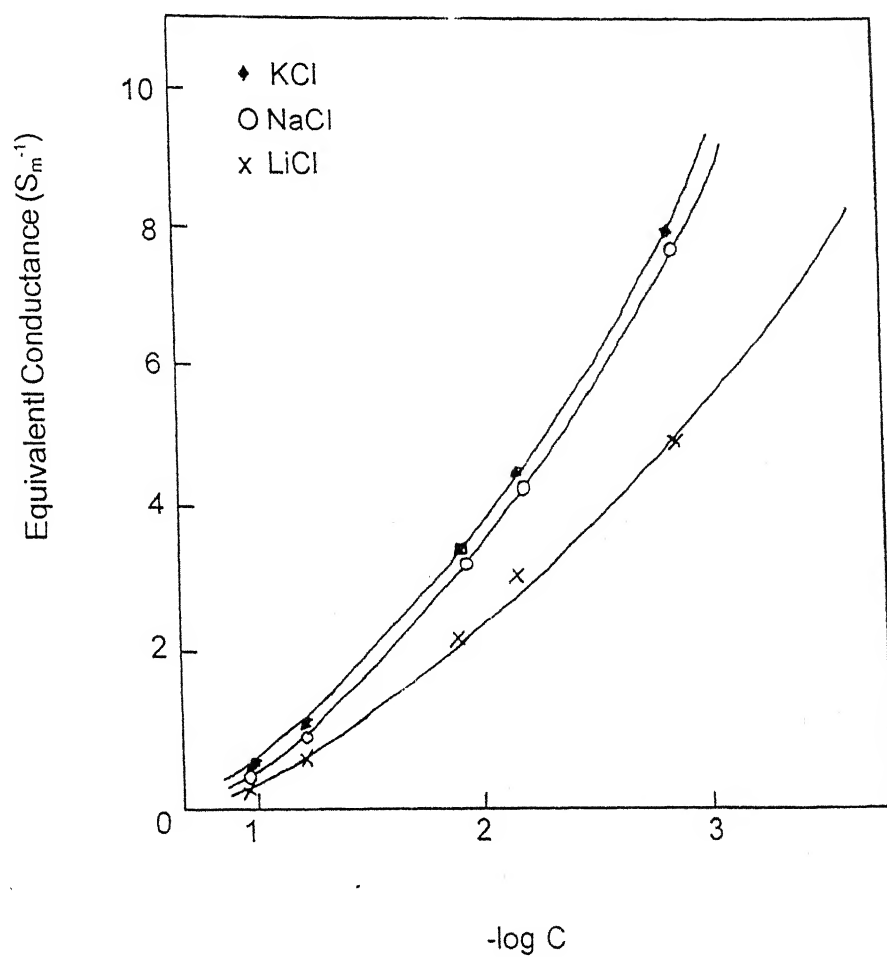


FIG. - 19

Typical plots of equivalent conductance (S_m^{-1}) vs. $-\log C$
for cobalt sulphide membrane

Table 15

Values of the selectivity K_{ji} derived from intramembrane permeability ratio and the ratio of electrical conductivities at various electrolyte concentration for nickel sulphide membrane.

Selectivity Concentration / Mol L ⁻¹	K_{NaK}	K_{LiK}	K_{LiNa}
$1 \times 10^{-1} / 1 \times 10^{-1}$	0.62	0.33	0.6
$5 \times 10^{-2} / 5 \times 10^{-2}$	0.74	0.46	0.76
$1 \times 10^{-2} / 1 \times 10^{-2}$	1.10	0.72	0.93
$5 \times 10^{-3} / 5 \times 10^{-3}$	1.25	0.76	0.99
$1 \times 10^{-3} / 1 \times 10^{-3}$	1.80	1.43	1.52

Table 16

Values of the selectivity K_{ji} derived from intramembrane permeability ratio and the ratio of electrical conductivities at various electrolyte concentration for cobalt sulphide membrane.

Selectivity Concentration / Mol L ⁻¹	K_{NaK}	K_{LiK}	K_{LiNa}
$1 \times 10^{-1} / 1 \times 10^{-1}$	1.06	0.53	0.56
$5 \times 10^{-2} / 5 \times 10^{-2}$	1.20	0.63	0.67
$1 \times 10^{-2} / 1 \times 10^{-2}$	1.25	0.73	0.72
$5 \times 10^{-3} / 5 \times 10^{-3}$	1.60	0.87	1.03
$1 \times 10^{-3} / 1 \times 10^{-3}$	2.07	1.33	1.04

has often been used to derive the value of K_{ij}^{Pot} of membrane electrolyte system.

$$E = \frac{nRT}{F} \ln[(a_i')^{1/n} + (K_{ij}^{Pot} a_j')^{1/n}] / [(a_i'')^{1/n} + (K_{ij}'')^{1/n}] \quad [15]$$

where

$$K_{ij}^{Pot} = K_{ij} (\bar{U}_j / \bar{U}_i)^{1/n}$$

If $n=1$ and the concentrations on ["] side are held constant then eqn. [15] gives

$$E = cons + (RT/F) \ln[a_i' + (K_{ij}^{Pot} a_j')] \quad [16]$$

The equation [16] is considered a normal form for ideal behaviour of ion selective electrode responses to species i and j . If the response for cation is more positive for solutions of species i than for j at equal activities then K_{ij}^{Pot} is than unity and the electrode is more sensitive to i to j [23]. Equation [16] has been used in various ways for the evaluation of potentiometric selectivity constant K_{ij}^{Pot} . Various aspects of eqn. [16] for the evaluation of K_{ij}^{Pot} were reviewed by Lakshminarayanaiah [49]. Mixture methods based on eqn. [16] were first developed and used extensively by Lengyel and Blum [50] and later by Eisenman [51]. Srinivasan and Rechnitz [52] examined several methods for the determination of K_{ij}^{Pot} while Pungor and Toth [53, 54] strongly recommended another form of the mixutre method. The titration procedure of Dole [46] which was modified and improved by Buck et al. [47,48]. This method provides extensive sets of data for the determination of K_{ij}^{Pot} [apparent]. In this method a set of mixture response potentials ΔE were measured and the selectivity coefficient were calculated using the equation

eqn. [17].

$$\ln K_{ij}^{Pot} (apparent) = \ln \{ \exp[\Delta E_{ij} - E_i] / S \} - 1 \} - \ln(a_h / a_u) \quad [17]$$

where S is the slope of the pure a_i response curve as shown in Figs. 20 and 21.

Electrical potentials ΔE_{ij} across both parchment supported membranes in the electrochemical cell of the type shown above were measured by taking fixed concentrations of both the primary ions [i.e., i and j] on the side ['] and varying the concentration of the ionic species i and j on the side ["] whereas, in another experiment only one ion either i or j on the side ["] at different concentration was taken and thus electrical potentials ΔE_i or ΔE_j were plotted against $\log a_i$ or a_j as shown in Figs. 20 and 21. Parallel straight lines depicted in figures were obtained which indicates the ideal behaviour of the membrane system. The slope S of the line was used to derive the values of K_{ij}^{Pot} [apparent] using eqn. [17]. In this way, the values of the K_{ij}^{Pot} obtained for both the parchment supported nickel and cobalt sulphide membranes using various 1:1 electrolytes are given in Tables 17 and 18.

Parchment supported nickel and cobalt sulphide membranes in contact with various 1: 1 electrolyte solutions were thus considered as homogeneous membrane elements with charged rigid capillary structure or gels having a diameter large as compared to the thickness of the electrical double layer at the walls [9,10,14] in accordance with the classical fixed charge theory of Teorell [9], Meyer and Sievers [10], Schaep et. al. [55], Mohammad et. al. [56], Ariza et. al. [57], Kobatake and coworkers [58-61] and Tasaka and coworkers [37] etc. Flow of electrolyte by diffusion because of the presence

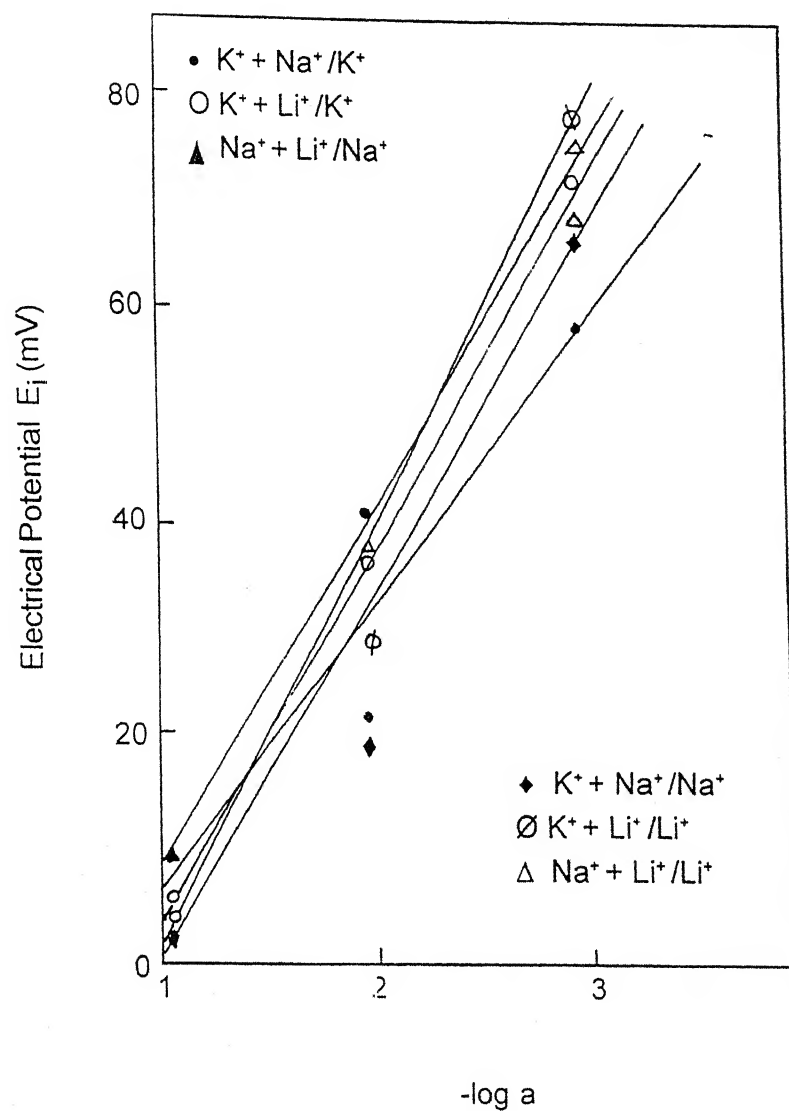


FIG. - 20

Plots of Electrical potential E_i (mV) v.s log a
 for nickel sulphide membrane

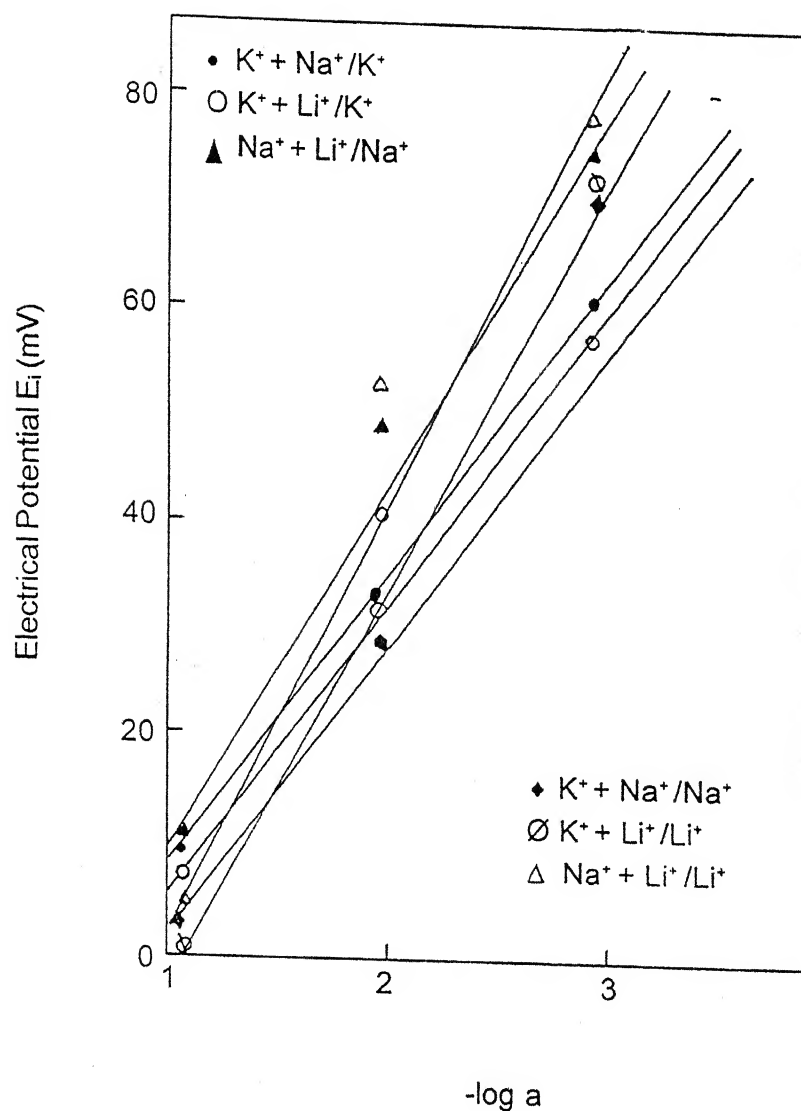


FIG. - 21

Plots of Electrical potential E_i (mV) v.s log a
 for cobalt sulphide membrane

Table 17

Values of potentiometric selectivity constant $[K_{ij}^{\text{Pot}}]$ for the nickel sulphide membrane at various electrolyte concentration.

Selectivity constant Concentration / Mol L ⁻¹	K_{K-Na}	K_{K-Li}	K_{Na-Li}
1×10^{-1}	0.64	0.35	0.49
1×10^{-2}	1.10	1.20	1.34
1×10^{-3}	4.01	5.20	2.18

Table 18

Values of potentiometric selectivity constant $[K_{ij}^{\text{Pot}}]$ for the cobalt sulphide membrane at various electrolyte concentration.

Selectivity constant Concentration / Mol L ⁻¹	K_{K-Na}	K_{K-Li}	K_{Na-Li}
1×10^{-1}	0.82	0.49	0.60
1×10^{-2}	1.10	1.20	1.40
1×10^{-3}	3.50	4.01	3.20

of a net charge on the membrane gives rise to membrane potential which regulates the flow of electrolyte by increasing the speed of the slow moving ion and also by decreasing the speed of the fast moving ion. The electrical double layer at the membrane solution interface seems to control the ion permeation as suggested by Tien and Ting [62] for bilayer membranes and our findings with inorganic precipitate nickel and cobalt sulphide membranes. Perfect Donnan exclusion of coions was realized in the dilute limit of the external solution and that the selectivity sequence of the membranes for alkali metal ions was

$$K^+ > Na^+ > Li^+$$

SELECTIVITY IN TERMS OF ENERGETIC TERMS :

In order to substantiate our findings and further to understand the selectivity of membranes in energetic terms, the values of various activation parameters have been evaluated on the basis of rate theory. The need for the use of rate theory has been felt because, electrical measurements carried out for assessing selectivity involve kinetic contributions to the permeation process and their explanation can not be expected to be given rigorously in terms of equilibrium energetics concepts. The rate theory describes any process from diffusion to chemical reaction in terms of elementary jumps over energy barriers, and can be used to represent the processes of permeation in as much detail or with as much accuracy as desired. The permeant encounters energy maxima [barriers] and minima [wells] in its journey from one side of the membrane to the other. The energy maxima represents the energies of the transition states, and diffusion past these

unfavourable loci that can be represented by single jumps over the corresponding barrier. The progress over each barrier is proportional to the number of ions attaining the energy needed to cross the barrier. The rate constant K_i for crossing over a barrier is related to standard Gibb's Free energy of activation,

$$k_i A_i \exp (-\Delta F^* / RT) \quad [18]$$

where A_i is the frequency of attempted hops. The ΔF^* is related to enthalpy $[\Delta H^*]$ and entropy $[\Delta S^*]$ of activation as

$$\Delta F^* = \Delta H^* - T \Delta S^* \quad [19]$$

ΔH^* and ΔS^* can be evaluated with the help of specific conductance, (π) , by making the use of the following relationship:

$$\pi = RT/Nh \exp [-\Delta H^*/RT] \exp [\Delta S^*/R] \quad [20]$$

The obtained values of ΔH^* can be used to evaluate the Arrhenius activation energy, E_a , using the following eqn. [21]

$$E_a = \Delta H^* + RT \quad [21]$$

To use equation [20], $\log \pi nH / RT$ has been plotted against $1/T$ as shown in Figs. 22 and 23. The straight line plots confirm the applicability of this equation to our model system and allow the calculation of ΔH^* and ΔS^* from the slopes and intercepts of the linear plots. The parameters so evaluated have been used to calculate the magnitude of ΔF^* and E_a with the help of eqns. [19] and [21], respectively. The results of these calculations are summarized in Tables 19 and 20.

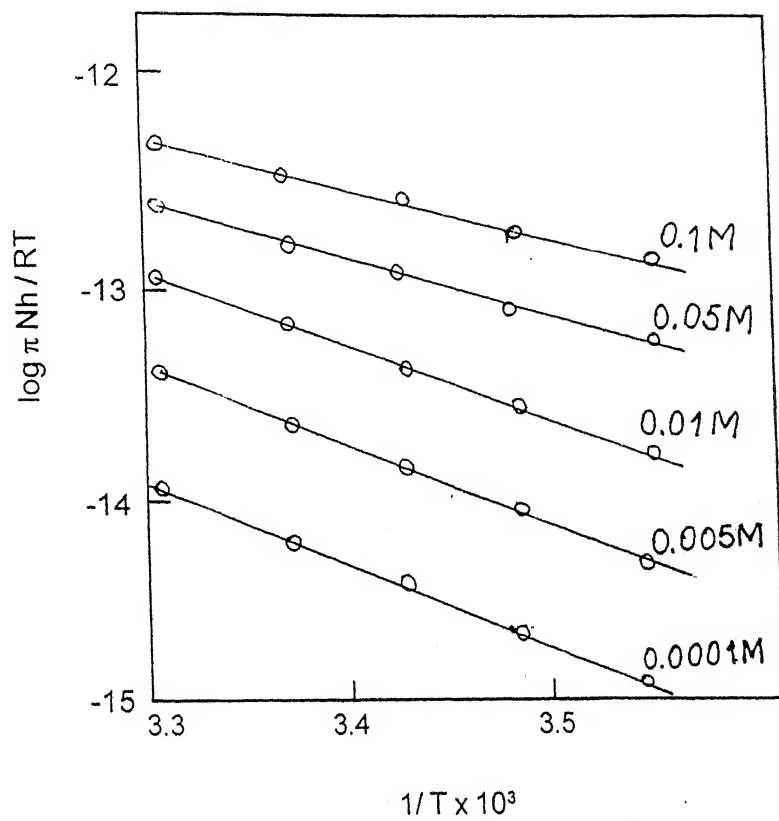


FIG. - 22

Plots of $\log \pi N_h / RT$ vs. $1/T$ for nickel sulphide membrane.

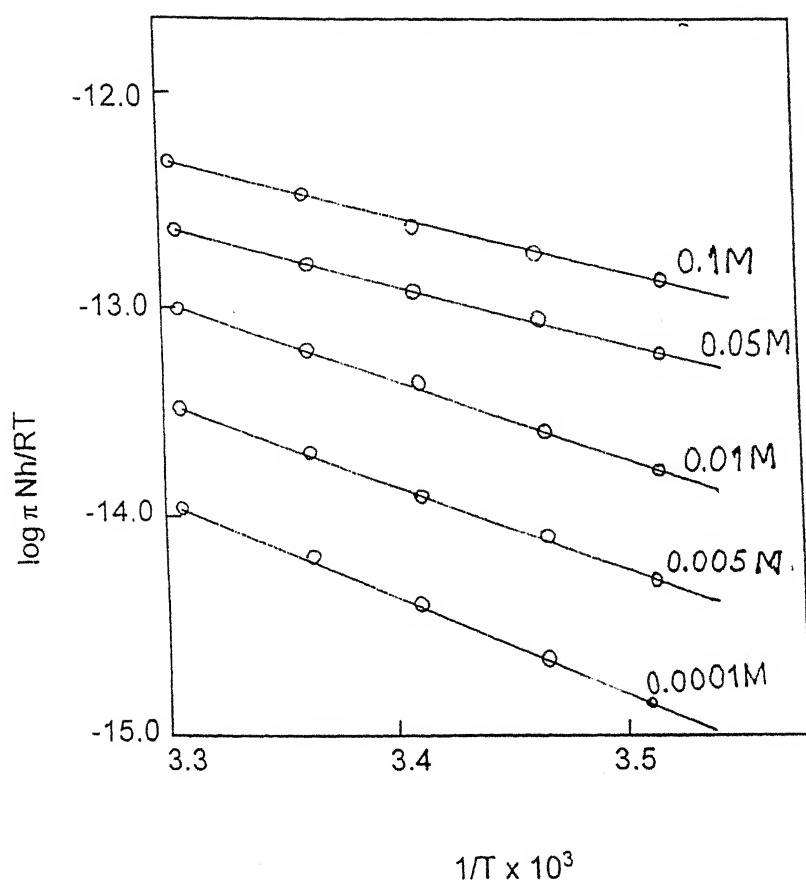


FIG. - 23

Plots of $\log \pi N_h / RT$ vs. $1/T$ for cobalt sulphide membrane.

Table 19

The values of thermodynamic activation parameters evaluated on the basis of theory of absolute reaction rates.

Membrane	Nickel Sulphide				
Electrolyte	Concentration n	E _a	ΔF [‡]	ΔH [‡]	- ΔS [‡]
KCl	1x10 ⁻¹	1.30	10.80	1.32	14.30
	5x10 ⁻²	2.10	13.65	2.75	15.21
	1x10 ⁻²	4.11	15.92	3.90	16.70
	5x10 ⁻³	5.65	17.10	5.25	17.50
	1x10 ⁻³	7.10	18.75	6.50	20.70
NaCl	1x10 ⁻¹	1.13	11.8	1.11	19.20
	5x10 ⁻²	2.94	13.27	2.17	19.82
	1x10 ⁻²	4.17	15.22	3.32	20.16
	5x10 ⁻³	5.35	17.23	4.97	21.37
	1x10 ⁻³	6.94	18.24	6.23	23.13
LiCl	1x10 ⁻¹	1.01	11.60	1.01	20.0
	5x10 ⁻²	2.91	11.13	2.73	21.32
	1x10 ⁻²	4.13	15.53	3.50	22.75
	5x10 ⁻³	5.23	17.14	4.75	23.35
	1x10 ⁻³	6.17	17.43	9.97	24.25

Table 20

The values of thermodynamic activation parameters evaluated on the basis of theory of absolute reaction rates.

Membrane	Cobalt Sulphide				
Electrolyte	Concentration n	E_a	ΔF^\ddagger	ΔH^\ddagger	$-\Delta S^\ddagger$
KCl	1×10^{-1}	1.50	11.0	1.37	14.0
	5×10^{-2}	2.40	13.72	2.81	15.14
	1×10^{-2}	4.15	15.98	3.96	16.63
	5×10^{-3}	5.71	17.23	5.32	17.08
	1×10^{-3}	7.40	18.82	6.80	20.63
NaCl	1×10^{-1}	1.21	11.3	1.16	17.5
	5×10^{-2}	2.98	13.32	2.25	18.22
	1×10^{-2}	4.23	15.41	3.42	19.34
	5×10^{-3}	5.41	17.36	5.13	20.45
	1×10^{-3}	6.70	18.27	6.10	21.37
LiCl	1×10^{-1}	1.01	11.80	1.07	20.20
	5×10^{-2}	2.98	11.19	2.84	21.41
	1×10^{-2}	4.27	15.67	3.76	22.87
	5×10^{-3}	5.63	17.28	4.88	23.52
	1×10^{-3}	6.38	18.83	9.96	24.45

The size dependence of the magnitude of E_a , ΔF^* and ΔH^* shows that a larger ion has more difficulty in crossing the membrane than a smaller one. This type of variation can be explained by considering the location of energy peaks and wells and also by comparing the heights of energy barriers [i.e., the difference between outer wells and peaks]. It has been found that the larger ion encounters a bigger entrance barrier lying very close to the surface of the membrane. The entrance barrier for the smaller ion is not only to lesser height but also lies farther in [30]. The location of the outermost well has been assumed to be the same for all the species, while that of the inner well is much farther in for the smaller ion than the larger ones. Keeping in mind these facts, it can be argued that the magnitude of the above mentioned activation parameters should be higher for larger ions than for smaller ones.

The magnitude of ΔS^* indicates the mechanism of flow, and has been interpreted in a number of ways. The low negative values of ΔS^* found for ion permeation through the parchment membrane used in the present investigation are attributable to electrolyte diffusion with partial immobilization in the membrane, the partial immobility increasing with the increase of density of charge on the permeant. This conclusion is in good agreement with the most recent findings of Marcus [63], who established that the translational immobilization entropy of solvents follows the sequence $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ resulting the selectivity sequence of the membranes for alkali metal ions as :



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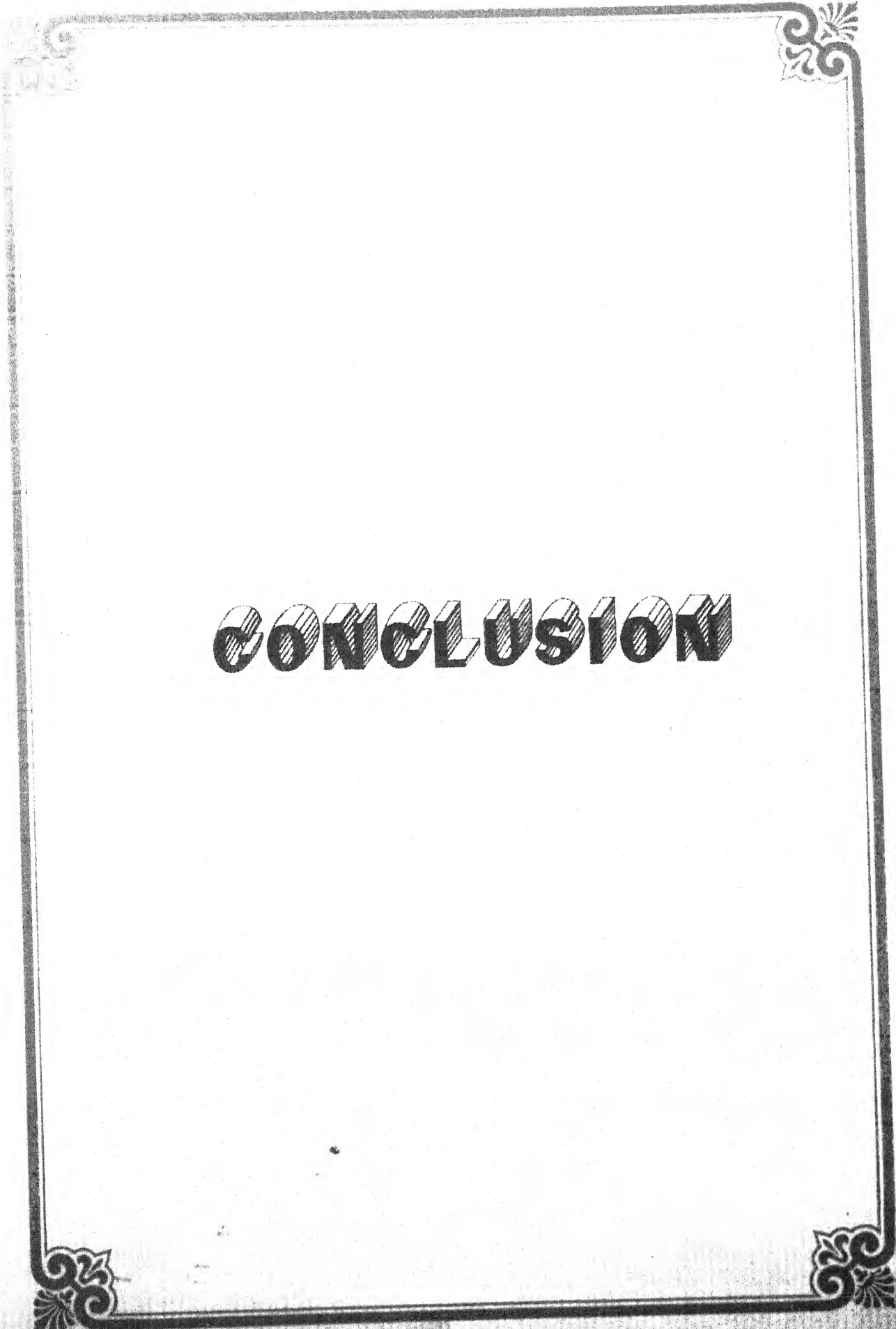
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CONCLUSION

CONCLUSION

Transport phenomena under the head of "Diffusion of electrolytes" were found very much challenging to recently burning problems. After the fabrication of the parchment supported inorganic precipitate membranes of nickel and cobalt sulphide separately, membrane potential and membrane resistance were observed experimentally at different temperatures after definite intervals of time in order to study of permeation of electrolytes as cations/anions across both the membranes with the help of recently developed theories. The membrane resistance R_m of both the membranes at any given time for metal ions and alkali earth metal ions in sequence as : $Li^+ > Na^+ > K^+$ and $Ba^{++} > Ca^{++} > Mg^{2+}$ and also of aluminum ion refers that very few coions are in membrane phase. On the other hand, the effect of charge on cation is seen an important factor towards the mobility of cations across both the parchment supported membrane. Besides of the membrane potential, the sequence of monovalent cations i.e. $Li^+ > K^+ > Na^+$ and di-valent/tri-valent cations i.e. $Al^{3+} > Ba^{++} > Ca^{2+} > Mg^{2+}$ also points towards the adsorption of these ions on membranes matrix. The slight changes of membrane potential (E_m) and membrane resistance (R_m) are considered due to the nature of ions and membrane, affected during the adsorption.

The values of diffusion rate dQ/dt for various cations of both the membranes calculated from the values of membrane potential (E_m) and

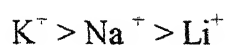
membrane resistance (R_m) are found slower than in free solution which is the attribution of interaction of diffusing species with the fixed charge groups on the membrane matrix. The diffusion rate sequence of cations diffusing through both the membranes was $K^+ > Na^+ > Li^+$ and $Mg^{2+} > Ca^{2+} > Ba^{2+} > Al^{3+}$, which on the basis of Eisenman Sherry model of membrane selectivity can be seen, because of weak field strength of charge groups attached to the membrane matrix. However, use of absolute reaction rate theory towards the evaluation of thermodynamic membrane parameters in which negative value of entropy change, ΔS^\ddagger , indicates the mechanism of flow of coions /counter ions as interstitial permeation of the membrane (Minimum Chain loosening) with immobilization in the membrane (small zone of disorder). Here, both membranes show same behaviour towards the diffusion of different electrolytes. Hence, it is concluded that membrane solution interface is the rate limiting step for permeation.

The chapter "Charge Density of Membranes" is also a part of study of characterising the membranes. In this work, parchment supported membrane made of nickel sulphide and cobalt sulphides by the method of interaction used to observe membrane potential values (E_m) across both the membranes. When they are used to separate electrolyte solution of different concentrations, indicate the presence of charge on membrane matrix. The change of (E_m) values in reverse order of electrolyte concentrations suggests the reversal of membrane charge and selectivity of sulphide membranes which is not seen in our earlier

findings. However, it is an interesting indication for both nickel and cobalt sulphide membranes that the membranes are cation selective when separating the dilute solutions and anion selective while separating the concentration solutions.

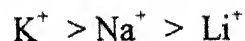
On the other hand, the transference number (t_-) of co-ions through the membranes increases from high to lower concentration of electrolytes further indicates the preferential salt adsorption which is infact, the charge distribution on membrane sites in turn. Simultaneously, the apparent transference number (t_{app}) approximately similar to (t_-) for co-ions are seen important factors for the evaluation of effective fixed charge density (X) values. However, the estimation of permselectivity P_s values with the support of t_- and t_{app} both, were seen very effective towards X determination. At the last, the thermodynamically fixed charge density (X) values of both the membrane system individually by using different methods were found low, which indicated that both the membranes have stable fixed charge distribution in their phase.

Parchment supported membranes of nickel sulphide and cobalt sulphide in Chapter - III, were used as model membranes to study their selectivity of metal ions. Initially experimentally observed values of membrane potential and the values of effective fixed charge density evaluated thermodynamically, indicated the membrane selectivity and its order in the light of Eisenman and Horn for both the membrane as:



Further, to substantiate the findings of selectivity sequence, the following methods like, (a) Biionic method: interposing the membrane between two electrolyte solution of same concentration and on the other hand, by varying the concentration of an electrolyte on one side and keeping of other side constant and (b) Mixture Method: in which the solutions of the mixture of two electrolytes at a time were separated by the membranes were employed. After having observed the biionic potential values across both the membranes experimentally along with the electrical membrane conductance and applying the various recently developed theories of membrane selectivity, the previously reported order of the selectivity was confirmed. In this way, the author characterised both the membranes for their selectivity of the metal ions using effective fixed charge density, biionic potential and conductivity measurements.

In the last, a major advancement towards membrane selectivity on the behalf of recently developed theory is that, equilibrium selectivity among alkali metal cations could also be explained in energetic terms, as the differences in Gibb's free energy lost in dehydrating the ions and that gained by integration with binding sites. In this way, the selective membrane behavior in terms of thermodynamic activation parameters, evaluated utilizing the theory of absolute reaction rate was also found as :



The size dependence of the magnitude of various thermodynamic activation

parameters shows that the larger ion which faces a bigger entrance barrier lying very close to the surface of the membrane has more difficulty in crossing the membrane than the smaller ions for which the entrance barrier is not only lower but also lies further in. The negative values of entropy of activation are an indication of the fact that electrolyte diffusion takes place with partial immobilization in the membrane. Thus all the methods not only confirm the existence of the membranes but also reflects the importance on the basis of their character.



SUMMARY

SUMMARY

Transport phenomena occurring across parchment supported membranes have been thoroughly investigated by taking into account the following aspects, namely (i) ionic transport, (ii) membrane potential, (iii) electrical conductivity, (iv) ionic distribution equilibria and (v) spatial distribution of ions and the potential within the membrane.

The work described in the thesis has been divided into following three parts.

Part I deals with the preparation of new system of parchment supported cobalt and nickel sulphide membranes and the studies of diffusion of a number of 1:1, 2:1 and 3:1 type of electrolytes through them. Various membrane parameters, namely, membrane potential E_m , cationic potential E_c^+ and membrane resistance R_m etc. have been determined using the electrolytes at different concentrations by electrometric method. The diffusion rates were computed using the recently developed equation by Kittleberger based on the simple laws of electrolysis and utilizing the derived membrane parameters. The diffusion rate sequence derived at $25 \pm 0.1^\circ\text{C}$ was as follows: $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ and $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Ba}^{2+} > \text{Al}^{3+}$. The diffusion rate sequence of the membrane for various uni, bi and trivalent cations were found to be primarily dependent on the differences in the hydration energies of Counterions in the external solution. On the basis of Eisenman-Sherry theory of membrane selectivity, this diffusion rate

sequence of alkali metal cations point towards the weak field strength of the fixed charge groups on the membrane matrix.

Various membrane transport parameters at different temperatures were also evaluated and the energy of activation E_a for the diffusion of electrolytes were calculated. It was found that the values of E_a for diffusion through the membranes were higher than those found for diffusion in free solution.

The theory of absolute reaction rates was applied for the diffusion process and the various activation parameters namely, enthalpy of activation ΔH^\ddagger , free energy of activation ΔF^\ddagger , and entropy of activation ΔS^\ddagger were evaluated. The values of ΔS^\ddagger were found to be negative indicating thereby that the diffusion takes place with partial immobilization in the membrane phase. The relative partial immobility was found to increase with increase in the valance of the ion constituting the electrolyte. A formal relationship between ΔH hydration, ΔF hydration and ΔS hydration of cations with the corresponding values of ΔH^\ddagger , ΔF^\ddagger and ΔS^\ddagger for diffusion was also found to exist for these membranes.

Part II deals with the characterization and evaluation of effective fixed charge density of parchment supported nickel and cobalt sulphide membranes from membrane potential measurements using various 1:1 electrolytes at different concentrations. The following methods: (i) Teorell-Meyer and Sievers method, (ii) the methods developed by Kobatake and co-workers and (iii) the most recently developed method of Tasaka et al. based on the principles of irreversible thermodynamics for the evaluation of charge density values were utilized.

The value of membrane potential measured across cobalt and nickel sulphide membrane with the use of the chlorides of K^+ , Na^+ and Li^+ were positive of all electrolyte concentrations when the membrane was used to separate dilute solutions of the electrolytes (dilute solution side taken as positive). The membrane potential values of both the membranes increase from higher to lower concentration of electrolytes.

For the evaluation of effective fixed charge density Teorell-Meyer and Sievers (TMS) derived a theoretical equation for membrane potential when a charged membrane separates different concentrations of an electrolyte by considering a diffusion potential within the membrane and two interfacial potentials at the membrane solution interfaces. The membrane potential equation thus derived has been generally accepted and widely used for the evaluation of effective fixed charge density and mobility ratio of the ions within the membrane by the plotting method. The method gave quite satisfactory results.

Kobatake, Nozaki and others derived the equation for membrane potential on the fixed charge concept by utilizing a number of basic assumptions. The two limiting forms of the equation were derived and used for the evaluation of fixed charge density of the membranes. It was interesting to note that the theoretical predictions were borne out quite satisfactorily by our experimental results with both the membranes used for the investigations.

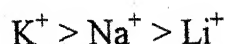
Another equation for membrane potential derived by Kobatake and Kamo, similar to the TMS equation was also used for the evaluation of thermodynamically effective fixed charge density of the membranes. This method involves the use of apparent transference number of coions and permselectivity P_s of the membranes. In this method, permselectivity

calculated from apparent transference number was plotted against $\log (C_1+C_2)/2$, the concentration at which P_s becomes $1/\sqrt{5}$ gave the value of the thermodynamically effective fixed charge density of the membrane.

Most recently Taksaka, Nagaswa and Co-workers derived some new equation for membrane potential when a charged membrane separates two solutions of an electrolyte based on the principles of the irreversible thermodynamics. At sufficiently high electrolyte concentrations the equation reduces to a suitable form which is used for the evaluation of effective fixed charge density of the membrane by the plotting method. Thus the values of effective fixed charge densities evaluated from different methods were identical which not only confirm the stability of the membranes but also recognize the recently developed membrane theories.

The chapter III of the thesis describes the selectivity of metal ions (Cations) and their order, of the parchment supported nickel and cobalt sulphide membrane respectively.

Initially, on the basis of membrane potential values observed experimentally across both the membranes, the selectivity and its sequence was found as.



Some theoretical equations based on the principles of non-equilibrium thermodynamics derived by Kobatake and co-workers for the charged membranes were found to evaluate the effective fixed charge density values of both the membrane electrolyte system. Various thermodynamic membrane parameters were evaluated using the values of membrane potential in these derived equations. With the help of these thermodynamic

membrane parameters, the effective fixed charge density against the 1:1 electrolytes of both the membrane were evaluated. The values of apparent transference number t_{app} and the per-selectivity P_s have been important factors during the electrochemical characterization of the membranes. Another theory developed by Tasaka and co-workers has also been used in the evaluation of magnitude of fixed charge ϕX . Since the values of ϕX thus obtained were quite low and thus membranes were expected to have low electrostatic field strength of the fixed charge sites. For this situation, following the Eisenman and Horn, selectivity sequence of metal ions was proposed.

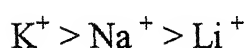
$$K^+ > Na^+ > Li^+$$

Under the heading of bi-ionic method the values of bi-ionic potential across both the membranes using various combinations of 1:1 electrolytes at different concentrations were measured. The intramembrane permeability ratio values of cations were obtained by the plotting method. Conductivity values of membranes were observed experimentally in order to evaluate selectivity of the membrane using the pre-determined values of the intramembrane permeability ratio. The sequence of selectivity of metal ion in the membranes phase again was found as.

$$K^+ > Na^+ > Li^+$$

which on the basis of the Eisenman sherry model of membrane selectivity points towards the weak field strength of the charge groups attached of the membrane matrix. Perfect Donnan exclusion of co-ions was realised in the dilute limit of the external solution.

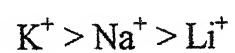
The mixture method is used to assess the selectivity sequence of the membranes for the cations by evaluating the values of potentiometer selectivity constant K_{ij}^{Pot} of the membranes. First of all, the mixture methods were developed and were used extensively by Iengyl and Blum and later by Eisenman, Srinivasan and Rechnitz for the determination of K_{ij}^{Pot} . Pungner and Toth recommended strongly the titration procedure of Dole of the matrix method which was modified and improved by Buck et. al., which provided the extensive sets of data for the determination of K_{ij}^{Pot} . In this method a set of mixture response potential was measured by taking fixed concentrations of both the primary ions (i.e. i and j) on one side while varying the concentration of ionic species (i and j on the other side). The values of K_{ij}^{Pot} were derived by using the slope of the lines which were obtained as a curve between electrical potential ΔE_i Or ΔE_j and $\log a_i$ $\log a_j$. Thus on the basis of K_{ij}^{Pot} values the selectivity sequence of metal ions was found as.



At last the selectivity sequence of the membrane for the metal ions was also tested in terms of the values of various activation parameters like E_a , ΔF^* , and ΔS^* predicted on the basis of rate theory.

The magnitude of ΔS^* represents the mechanism of flow and has been interpreted in a number of ways. The negative values of ΔS^* found for ion permeation are attributed to electrolyte diffusion with partial immobilization in the membranes, the partial immobility increases with the increase of density of charge on the permeant. This conclusion is in good agreement

with the most recent findings of marcus, Who established that the translation immobilisation entropy of solvents follows the sequence.





PUBLICATION

LIST OF PUBLICATION

- 1- Studies with Inorganic Precipitate Membranes : Evaluation of Membrane Selectivity from Electrical Potential and Conductivity Measurement, J. Ind. Council of Chemist (in press).
- 2- Studies with model membranes, Test of recently developed membrane potential theories based on non-equilibrium thermodynamics, Ind. J. Chem. (Under Communication).